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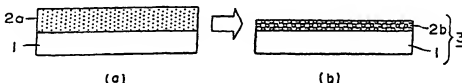
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(54) **METHOD FOR PRODUCING HIGH-PERFORMANCE MATERIAL HAVING PHOTOCATALYTIC FUNCTION AND DEVICE THEREFOR**

(57) Disclosed is a method and an apparatus are provided which can efficiently produce a functional material having a satisfactory level of photocatalytic activity. A photocatalyst coating composition comprising a photocatalytic metal oxide and/or a precursor of the photocatalytic metal oxide is coated on the surface of a substrate. The surface of the coated substrate is rapidly

heated to fix the photocatalytic metal oxide onto the surface of the substrate. This rapid heating can realize the production of a functional material having a satisfactory level of photocatalytic activity in an efficient manner. The apparatus, which can continuously carry out the rapid heating immediately after the production of the substrate, can produce the functional material having photocatalytic activity in an efficient manner.



**F I G. 1**

## Description

BACKGROUND OF THE INVENTIONField of the invention

[0001] The present invention relates to a process and an apparatus for producing a functional material having various types of excellent photocatalytic activity, such as antimicrobial (bactericidal) activity, deodorant activity, and antifouling activity, useful for waste water treatment, purification of harmful gases and the like.

Background Art

[0002] In recent years, environmental pollution, for example, water pollution created by domestic waste water, industrial waste water or the like, offensive odor, or contamination with bacteria, typified by MRSA, or mold in living spaces and working spaces has been increased and has become a social problem.

[0003] Photocatalysts have drawn attention as materials that, upon light irradiation, cause adsorption of oxygen molecules on bacteria, mold, and organic compounds, such as offensive odor components, or desorption of oxygen molecules therefrom and accelerate the decomposition (oxidation) of the organic compounds. A number of attempts have been made to fix a photocatalyst on the surface of a substrate to clean the surface of the substrate.

[0004] PCT/WO 96/29375 discloses that the surface of a photocatalyst-containing layer provided on the surface of a substrate exhibits high hydrophilicity (for example, a contact angle thereof with water of not more than 10 degrees) in response to photoexcitation of the photocatalyst. This property can be utilized to improve antifogging properties and ensuring of visibility of transparent members, such as glasses, lenses, and mirrors, to improve water cleanability and rainfall cleanability of the surface of articles and to improve other properties.

[0005] Functional materials utilizing the function of the photocatalyst have hitherto been produced by providing a coating liquid containing a photocatalytic metal oxide or a precursor of the photocatalytic metal oxide, coating the coating liquid, and drying or sintering the coating. For example, a titania sol prepared from a titanium alkoxide and an alcoholamine or a sol prepared by dispersing particles of  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SrTiO}_3$  or the like in an aqueous solvent has been coated onto the surface of a substrate followed by drying or sintering. More specifically, as disclosed in Japanese Patent No. 2517874, the production process of functional materials comprises: coating a titania sol onto a substrate; heating the coated substrate in such a manner that the temperature is gradually raised from room temperature to a final temperature of 600 to 700°C to perform firing, thereby fixing the photocatalyst onto the substrate.

SUMMARY OF THE INVENTION

[0006] The present inventors have now found that functional materials having satisfactory photocatalytic activity can be efficiently produced by rapid heating. They have further found that rapid heating immediately after, that is, successively from, the production of the substrate can realize the production of functional materials having photocatalytic activity in more efficient manner. The present invention has been made based on such finding.

[0007] Accordingly, it is an object of the present invention to provide a process and an apparatus for producing a functional material having a satisfactory level of photocatalytic activity.

[0008] According to one aspect of the present invention, there is provided a process for producing a functional material having photocatalytic activity, comprising the steps of: coating a photocatalyst coating composition comprising a photocatalytic metal oxide and/or a precursor of the photocatalytic metal oxide onto the surface of a substrate; and

rapidly heating the surface of the coated substrate to fix the photocatalytic metal oxide onto the surface of the substrate.

[0009] According to another aspect of the present invention, there is provided an apparatus for producing a functional material having photocatalytic activity, said apparatus comprising at least

coating means for coating a photocatalyst coating composition comprising a photocatalytic metal oxide and/or a precursor of the photocatalytic metal oxide onto the surface of a substrate and heating means for rapidly heating the surface of the coated substrate to fix the photocatalytic metal oxide onto the surface of the substrate.

[0010] According to the process and apparatus of the present invention, a photocatalytic metal oxide can be surely fixed in a short time on the surface of a substrate, and, in addition, a functional material can be obtained which has high surface smoothness, possesses high photocatalytic activity, and high abrasion resistance and chemical resistance. Furthermore, the process and apparatus of the present invention can reduce the size of the production apparatus used and can realize simplification of the production process and space saving. Furthermore, shortening of the time taken for heating can advantageously contribute to a reduction in cost and a reduction in the amount of the exhaust gas emitted.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figs. 1 (a) and (b) are diagrams illustrating an embodiment of the process for producing a functional material having photocatalytic activity according to the present invention, wherein a layer 2a of a photocatalyst

coating composition coated onto a substrate 1 is rapidly heated to form a thin layer 2b for imparting photocatalytic activity to the substrate 1;

[0012] Figs. 2 (a) and (b) are diagrams illustrating another embodiment of the process for producing a functional material having photocatalytic activity according to the present invention, wherein, upon rapid heating of a layer 2a of a photocatalyst coating composition and a layer 4a of a binder and a solvent coated on a substrate 1, the layer 2a is converted to a thin layer 2b for imparting photocatalytic activity to the substrate 1 while the layer 4a is converted to a layer 4b which has non-crosslinked oxygen and contributes to the development of hydrophilicity;

[0013] Fig. 3 is a diagram illustrating an embodiment of the apparatus for producing a functional material according to the present invention, which comprises: an apparatus for producing earthenware as a substrate, comprising a forming device 5, a glazing device 6, and a firing device 7; the apparatus of the present invention provided continuously from the apparatus for producing the substrate, the apparatus of the present invention comprising a coating device 8 for coating a photocatalyst coating composition, a rapid heating device 9, and a cooling device 10; and a carrying device 16 provided so that the substrate can be continuously carried through within each of the devices and through between the devices;

[0014] Fig. 4 is a schematic diagram showing the structure of the rapid heating device 9 shown in Fig. 3, wherein the rapid heating device 9 comprises a heating element 21, a heat-resistant material 22 which covers the heating element 21 and forms a heating space, carrying means 16 for holding the substrate 23, to be heated, within the heating space and carrying the substrate in a direction indicated by an arrow A in the drawing, a carry-in port 24 for carrying the substrate in the heating space, and a carry-out port 25 for carrying out the substrate from the heating space; and

[0015] Fig. 5 is a diagram showing another embodiment of the apparatus according to the present invention, having the same construction as the apparatus shown in Fig. 3 except that a preheater 11 for preheating the surface of the substrate before coating a photocatalyst coating composition and a drier 12 for drying the substrate coated with the coating composition are additionally provided.

## PREFERRED EMBODIMENTS OF THE INVENTION

### Process for producing functional material

#### (a) Substrate

[0016] The present invention relates to a process for producing a functional material having photocatalytic activity. By virtue of photocatalytic activity, various functions are imparted to substrates, and examples of such

functions include hydrophilicity, antimicrobial activity, antifouling properties, anti-algae properties, antifogging properties, conversion of NO<sub>x</sub>, and antistatic properties. Therefore, the "functional material" produced by the process according to the present invention refers to a material which, as a result that photocatalytic activity has been imparted, has come to possess at least one function among the above various functions. Substrates to which the production process of the present invention is applicable include metals, inorganic materials, organic materials, and composite of these materials. Specific examples thereof include interior materials, exterior materials, tiles, sanitary wares, tablewares, calcium silicate board, cement extruded boards and other building materials, ceramic boards, semiconductors and other new ceramics, insulators, glasses, mirrors, woods, and resins.

#### (b) Photocatalyst coating composition

[0017] According to the production process of the present invention, a photocatalyst coating composition to be coated onto the substrate is first provided. The photocatalyst coating composition comprises a photocatalytic metal oxide and/or a precursor of the photocatalytic metal oxide.

[0018] The term "photocatalytic metal oxide" used herein refers to a material which, upon exposure to light (excitation light) having higher energy (i.e., shorter wavelength) than the energy gap between the conduction band and the valence band of the crystal, can cause excitation (photoexcitation) of electrons in the valence band to produce conduction electrons and holes. The photocatalytic metal oxide decomposes an organic compound through a redox reaction, or come to have a very high level of hydrophilicity as a result of adsorption of water molecules in atmosphere. According to a preferred embodiment of the present invention, the photocatalytic metal oxide is selected from the group consisting of TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, SrTiO<sub>3</sub>, WO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub>.

[0019] According to the present invention, the photocatalyst coating composition may contain a precursor of the photocatalytic metal oxide. The term "precursor of the photocatalytic metal oxide" refers to a compound which can be converted to the photocatalytic metal oxide upon rapid heating described below. According to a preferred embodiment of the present invention, precursors of the photocatalytic metal oxide usable herein include compounds which contain at least one metal selected from the group consisting of titanium, zinc, tin, strontium, tungsten, bismuth, iron, and vanadium and, upon rapid heating described below, can be converted respectively to the corresponding photocatalytic metal oxides.

[0020] According to a preferred embodiment of the present invention, the photocatalyst coating composition further comprises a binder. The addition of the bind-

er is advantageous in that the photocatalytic metal oxide can be more strongly fixed onto the surface of the substrate. A specific example of preferred binders usable herein is, as described below, a mixture of at least one member, selected from the group consisting of, inorganic oxide particles, silicone resin film precursors capable of forming silicone resin films, and silica film precursors capable of forming silica films, with a solvent. Another examples of preferred binders include alkali silicates represented by formula  $Me_2O \cdot nSiO_2$  wherein Me represents an alkali metal, for example, water glass, potassium silicate, lithium silicate, sodium silicate, and silica. Further, mixtures of the above binders with silicon, aluminum, potassium, lithium, sodium, cesium, calcium, magnesium, titanium, phosphorus, boron, zirconium, lanthanides, such as cerium, or compounds of the above elements. Compounds of silicon, aluminum, potassium, lithium, sodium, cesium, calcium, magnesium, titanium, phosphorus, boron, zirconium, and cerium refer to compounds represented by formula  $MO$ ,  $MOH$ ,  $MX$ , or  $MOR$  wherein M represents the above element, X represents a halogen atom, and R represents an alkyl group. Specific examples of the these compounds include  $SiO_2$ ,  $SiO_3$ ,  $Si(OH)_3$ ,  $Al(OH)_3$ ,  $TiCl_4$ , and  $Ti(OC_2H_5)_4$ . Utilization of these mixtures as the binder can provide functional materials having good photocatalytic activity. More specifically, functional materials can be provided which have a high level of retention of hydrophilicity in dark places, and permit oil stains to be easily removed by water. Further, functional materials having negative surface charges can be obtained. Furthermore, functional materials having a short half value period (preferably not more than 10 sec) of surface charges can be provided. Furthermore, by virtue of high surface strength (according to a preferred embodiment of the present invention, a hardness of not less than 2H in terms of pencil hardness), functional materials possessing excellent chemical and physical resistance can also be provided.

[0021] A precursor of the alkali silicate may be used in combination with or instead of the alkali silicate. Precursors of the alkali silicate include hydroxides of lithium, potassium, sodium, and silicon.

[0022] According to a preferred embodiment of the present invention, the concentration of the photocatalytic metal oxide and/or the precursor of the photocatalytic metal oxide in the photocatalyst coating composition is preferably 0.001 to 35% by weight on a solid basis, more preferably 0.1 to 10% by weight. When the concentration is in the above range, a photocatalytic surface having good properties and good strength can be provided. Further, in this case, it is possible to provide functional materials the surface of which is even and smooth and has good gloss.

[0023] Further, the photocatalyst coating composition can produce a large amount of non-crosslinked oxygen on the surface of the functional material which will be described later. The term "non-crosslinked oxygen"

used herein refers to the following oxygen. In a large part of the binder component, M-OH, wherein M represents a metal element with specific examples thereof including silicon, titanium, aluminum, zirconium, tin, tantalum, and bismuth, is crosslinked upon rapid heating to form M-O-M bonds. This results in an increase in molecular weight, and the binder, together with the photocatalytic metal oxide, is fixed onto the surface of the substrate. In this case, a part of the M-OH is incorporated into the resultant polymer molecules and is present without forming the M-O-M bond. This part of the M-OH is ionically bonded to ion species (for example, sodium) present in the photocatalyst coating composition to give  $M-O^+X^-$  (wherein X represents a cation, such as sodium ion) which can be reversibly converted to M-OH. Further, the present inventors have found that, under rapid heating conditions described below, the M-O-M bond, upon contact with water molecules in the air, is dissociated into M-OH bond. In the present invention, M-OH and  $M-O^+X^-$  refer to non-crosslinked oxygen. The non-crosslinked oxygen has high affinity for water molecules and even functions to incorporate water molecules in the air into the substrate in its surface. Further, upon contact of the surface of the substrate with water, the non-crosslinked oxygen is likely to be bonded preferentially to water molecules rather to molecules which are present on the surface of the substrate before water is deposited thereon. This results in the replacement of molecules, which are present on the surface of the substrate before water is deposited thereon, with water molecules. Consequently, the molecules, which are present on the surface of the substrate before water is deposited thereon, are removed from the surface of the substrate. Thus, the presence of the non-crosslinked oxygen on the surface of the substrate contributes to the development of a very high level of hydrophilicity on the surface of the substrate through cooperation with the hydrophilicity created by the photocatalytic metal oxide. This very high level of hydrophilicity offers an advantage that not only hydrophilic stains or soils but also lipophilic stains or soils can be easily washed away with water.

[0024] According to a preferred embodiment of the present invention, the photocatalyst coating composition contains the binder in an amount of 0.001 to 100 parts by weight, more preferably 0.1 to 5 parts by weight, based on 1 part by weight of the photocatalytic metal oxide and the precursor of the photocatalytic metal oxide. When the amount of the binder and the amount of the photocatalytic metal oxide satisfy the above relationship, the temperature necessary for the rapid heating is not very high. Further, functional materials having good properties can be provided.

[0025] According to a preferred embodiment of the present invention, the photocatalyst coating composition may further comprise a metal and/or a metal oxide, for example, at least one member selected from the group consisting of copper, silver, nickel, iron, zinc, platinum, gold, rhodium, vanadium, chromium, cobalt, man-



ganese, tungsten, niobium, antimony, platinum group metals, and oxides of the above metals. A preferred example of the metal and the metal oxide is at least one member selected from the group consisting of particles of copper, silver, platinum, cobalt, iron, nickel,  $\text{Cu}_2\text{O}$ ,  $\text{Ag}_2\text{O}$ , gold, zinc, chromium, manganese, and molybdenum. The addition of the metal or the metal oxide to the photocatalyst coating composition results in the formation of a film which can kill bacteria and mold deposited on the surface thereof even in a dark place. Further, the addition of platinum metals, such as platinum, palladium, ruthenium, rhodium, iridium, and osmium, or oxides thereof is preferred because they can enhance redox activity of the photocatalyst and consequently can improve the decomposition of organic stains or soils and the decomposition of harmful gases or offensive odors. Another preferred example of the metal oxide is at least one member selected from the group consisting of oxides of silicon, aluminum, potassium, lithium, sodium, cesium, rubidium, and francium. The addition of these metal oxides can yield a film having improved hydrophilicity. In this case, the metal oxide may be added as having also functions of the binder.

[0026] According to a preferred embodiment of the present invention, the metal and the metal oxide are supported on the surface of the photocatalytic metal oxide. The metal and the metal oxide may be supported on the surface of the photocatalytic metal oxide, for example, by a method which comprises adding a metal salt, such as silver nitrate or copper acetate, to a sol of photocatalyst particles and irradiating the mixture with ultraviolet light or the like to previously photoreductively fix the metal onto the surface of the photocatalyst particles, a method which comprises fixing photocatalyst particles onto the surface of the substrate, coating a metal salt, such as silver nitrate or copper acetate, and irradiating the coating with ultraviolet light or the like, thereby supporting the metal onto the surface of the photocatalyst metal in a later stage, or a method wherein the photocatalyst is doped with the metal.

[0027] According to a preferred embodiment of the present invention, the photocatalyst coating composition further comprises a surfactant. The addition of the surfactant permits the photocatalyst coating composition to be evenly coated onto the surface of the substrate.

[0028] According to the most preferred embodiment of the present invention, the photocatalyst coating composition basically comprises:

- (1) a photocatalytic metal oxide;
- (2) at least one member selected from the group consisting of inorganic oxide particles, silicone resin film precursors capable of forming silicone resin films, and silica film precursors capable of forming silica films; and
- (3) a solvent.

[0029] The average crystallite diameter of the photocatalytic metal oxide is preferably not more than 100 nm. The upper limit of the average crystallite diameter is preferably about 20 nm, more preferably about 10 nm. The lower limit of the average crystallite diameter is preferably about 1 nm, more preferably about 3 nm. An average crystallite diameter of the photocatalytic particles in the above range enables the hydrophilification to be satisfactorily exhibited and, at the same time, makes it possible to prevent loss of transparency, of a surface with the composition applied thereto, derived from scattering of visible light caused by the particles.

[0030] Examples of inorganic oxide particles usable in the composition according to the present invention include: single oxides, such as silica, alumina, zirconia, ceria, yttria, boronia, magnesia, calcia, ferrite, amorphous titania, and hafnia; and composite oxides, such as barium titanate, calcium silicate, water glass, aluminosilicate, and calcium phosphate.

[0031] According to a preferred embodiment of the present invention, the inorganic oxide is preferably in the form of either an aqueous colloid using water as a dispersing medium or an organosol prepared by dispersing the inorganic oxide in a colloidal form in a hydrophilic solvent, such as ethyl alcohol, isopropyl alcohol, or ethylene glycol. In particular, use of colloidal silica is preferred.

[0032] The diameter of the inorganic oxide particle is not particularly limited. However, a particle diameter of about 5 to 50 nm in the form of an aqueous colloid or an organosol is preferred from the viewpoint of the gloss, turbidity, haze, transparency and the like of the final photocatalytically hydrophilifiable coating.

[0033] A preferred example of the silicone coating precursor, capable of forming a silicone coating, which may be used in the composition of the present invention is a siloxane represented by the average composition formula:



wherein R represents a member selected from the group consisting of a hydrogen atom and one or more organic groups;

X represents an alkoxy group or a halogen atom; and

p is a number satisfying  $0 < p < 2$  and q is a number satisfying  $0 < q < 4$ .

[0034] Another preferred example of the silicone coating precursor, capable of forming a silicone coating, which may be used in the composition of the present invention is a hydrolyzable silane derivative represented by the general formula:



wherein R is as defined above;

X represents an alkoxy group or a halogen atom;  
and  
p is 1 or 2.

[0035] In this case, the organic group represented by R refers to preferably an alkyl (more preferably an unsubstituted alkyl having 1 to 18 carbon atoms, most preferably an alkyl having 3 to 18 carbon atoms) or an aryl (preferably phenyl).

[0036] Specific examples of preferred hydrolyzable silane derivatives include methyltrimethoxysilane, methyltriethoxysilane, methyltripropoxysilane, methyltributoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, ethyltripropoxysilane, ethyltributoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, phenyltripropoxysilane, phenyltributoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, dimethyldipropoxysilane, dimethyldibutoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, diethyldipropoxysilane, diethyldibutoxysilane, phenyldimethyldimethoxysilane, phenyldimethyldiethoxysilane, phenyldimethyldipropoxysilane, phenyldimethyldibutoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, n-propyltripropoxysilane, n-propyltributoxysilane, γ-glycidyloxypropyltrimethoxysilane, and γ-acyloxypropyltrimethoxysilane.

[0037] The siloxane may be prepared by partial hydrolysis and dehydropolycondensation of the hydrolyzable silane derivative, or by dehydropolycondensation of a partial hydrolyzate of the hydrolyzable silane derivative with a partial hydrolyzate of tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, diethoxydimethoxysilane or the like.

[0038] The silicone resin prepared by partial hydrolysis or dehydropolycondensation of the above precursor according to the following method is represented by the following average composition formula:



wherein R is as defined above;

X is an alkoxy group or a halogen atom; and  
p is a number satisfying  $0 < p < 2$ .

[0039] The content of the precursor in the composition according to the present invention may be suitably determined. For example, in terms of the silica content based on one part by weight of the photocatalytic particle, the upper limit of the precursor content is preferably 10 parts by weight, more preferably 5 parts by weight, most preferably 1 part by weight, and the lower limit of the precursor content is preferably 0.05 part by weight,

more preferably 0.1 part by weight, and most preferably 0.2 part by weight.

[0040] The solvent contained in the composition according to the present invention is not limited so far as it can stably disperse the photocatalytic particles and the precursor and a hydrophilified surface is finally provided. Examples of solvents usable herein include water, an organic solvent, and a mixed solvent composed of water and an organic solvent. Water, an alcohol, or a mixed solvent composed of water and an alcohol is particularly preferred.

[0041] According to a preferred embodiment of the present invention, use of an alcohol, which has a molecular weight of 60 to 300, preferably 60 to 100, and is liquid at room temperature, is preferred.

[0042] Specific examples of preferred alcohols usable herein include methanol, ethanol, n-propanol, isopropanol, t-butanol, isobutanol, n-butanol, 2-methylpropanol, pentanol, ethylene glycol, monoacetone alcohol, diacetone alcohol, ethylene glycol monomethyl ether, 4-hydroxy-4-methyl-2-pentanone, dipropylene glycol, propylene glycol, tripropylene glycol, 1-ethoxy-2-propanol, 1-butoxy-2-propanol, 1-propoxy-2-propanol, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, and 2-butoxyethanol.

[0043] A preferred example of the silica coating precursor is a silicate represented by the average composition formula:



wherein X represents an alkoxy group or a halogen atom and q is a number satisfying  $0 < q < 4$ .

[0044] Another preferred example of the silica coating precursor is a tetrafunctional hydrolyzable silane derivative represented by the general formula:



wherein R is as defined above; and

X represents an alkoxy group or a halogen atom.

[0045] Specific examples of preferred tetrafunctional hydrolyzable silane derivatives usable herein include tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, and diethoxydimethoxysilane.

[0046] Specific examples of preferred silicates usable herein include partial hydrolyzates and dehydropolycondensation products of the tetrafunctional hydrolyzable silane derivatives.

[0047] Water, an alcohol and the like may be used as the solvent for the composition. Particularly preferred are liquid alcohols having a molecular weight of 60 to 300. Since the evaporation rate of these alcohols is suitably slow, at the time of coating of the composition, a variation in dispersibility of the composition due to the

evaporation of the solvent can be inhibited, making it possible to form a transparent, even coating.

[0048] Examples of suitable liquid alcohols having a molecular weight of 60 to 300 usable herein include n-propanol, isopropanol, t-butanol, isobutanol, n-butanol, 2-methylpropanol, pentanol, ethylene glycol, monoacetone alcohol, diacetone alcohol, ethylene glycol monomethyl ether, 4-hydroxy-4-methyl-2-pentanone, dipropylene glycol, propylene glycol, tripropylene glycol, 1-ethoxy-2-propanol, 1-butoxy-2-propanol, 1-propoxy-2-propanol, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monomethyl ether, and tripropylene glycol monomethyl ether.

[0049] The composition may comprise, in addition to the above components, a surfactant, a polymerization curing catalyst, a hydrolysis catalyst, a levelling agent, an antimicrobial metal, a pH adjustor, a perfume, a preservative and the like.

[0050] Polymerization catalysts usable herein include aluminum compounds, such as aluminum chelate, aluminum acetyl acetonate, aluminum perchlorate, aluminum chloride, aluminum isobutoxide, and aluminum isopropoxide; titanium compounds, such as tetraisopropyl titanate and tetrabutoxy titanate; basic compounds, such as sodium hydroxide, lithium hydroxide, potassium hydroxide, sodium methylate, sodium acetate, sodium formate, potassium acetate, potassium formate, potassium propionate, and tetramethyl ammonium hydroxide; amine compounds, such as n-hexylamine, tributylamine, diazabicycloundecene, ethylenediamine, hexanediamine, diethylenetriamine, tetraethylenepentamine, triethylenetetramine, ethanalamines,  $\gamma$ -aminopropyltrimethoxysilane,  $\gamma$ -aminopropylmethyldimethoxysilane,  $\gamma$ -(2-aminomethyl)-aminopropyltrimethoxysilane, and  $\gamma$ -(2-aminomethyl)-aminopropylmethyldimethoxysilane; tin compounds, such as tin acetyl acetonate, and dibutyltin octylate; metal-containing compounds, such as cobalt octylate, cobalt acetyl acetonate, and iron acetyl acetonate; and acidic compounds, such as phosphoric acid, nitric acid, phthalic acid, p-toluenesulfonic acid, and trichloroacetic acid.

[0051] Suitable hydrolysis catalysts usable herein include nitric acid, hydrochloric acid, acetic acid, sulfuric acid, sulfonic acid, maleic acid, propionic acid, adipic acid, fumaric acid, phthalic acid, valeric acid, lactic acid, butyric acid, citric acid, malic acid, picric acid, formic acid, carbonic acid, and phenol, the above catalysts having a pH of 2 to 5.

[0052] Levelling agents usable herein include diacetone alcohol, ethylene glycol monomethyl ether, 4-hydroxy-4-methyl-2-pentanone, dipropylene glycol, tripropylene glycol, 1-ethoxy-2-propanol, 1-butoxy-2-propanol, propylene glycol monomethyl ether, 1-propoxy-2-propanol, dipropylene glycol monomethyl ether, dipropylene glycol monomethyl ether, and tripropylene glycol monomethyl ether.

#### (c) Coating of photocatalyst coating composition onto substrate

[0053] According to the process of the present invention, the photocatalyst coating composition is coated onto a substrate. Examples of suitable coating methods include spray coating, dip coating, flow coating, spin coating, roll coating, brush coating, and sponge coating. According to a preferred embodiment of the present invention, the photocatalyst coating composition is coated onto the substrate by spray coating.

[0054] According to a preferred embodiment of the present invention, the surface of the substrate is preheated before coating of the photocatalyst coating composition. The preheating of the substrate may be carried out by heating the surface of the substrate to 20 to 400°C. The preheating of the substrate is advantageous in that, upon coating of the photocatalyst coating composition onto the surface of the preheated substrate, the photocatalyst coating composition evenly spreads and yields an even coating.

[0055] According to a preferred embodiment of the present invention, the surface of the substrate coated with the photocatalyst coating composition may be dried before rapid heating. Rapid heating, which will be described later, applies a large heat value to the substrate. Presence of excess water or solvent component on the substrate leads to a fear of the smoothness of the surface of the substrate being lost as a result of rapid evaporation of water or the solvent component and the like due to a rapid temperature change. Therefore, in some cases, preferably, excess water or solvent component is previously removed by drying. The drying may be carried out by air blasting or heating.

[0056] Fig. 1 (a) is a schematic diagram showing an assembly comprising a layer 2a of a photocatalyst coating composition coated onto a substrate 1. Upon rapid heating described below, the photocatalyst coating composition layer 2a is brought to a thin layer 2b which functions to impart photocatalytic activity to the substrate 1. Thus, a functional material 3 having photocatalytic activity is obtained (Fig. 1 (b)).

[0057] According to a preferred embodiment of the present invention, the photocatalyst coating composition may be coated onto the surface of the substrate so as to form a stacked or multi-layered coating. Specifically, an identical photocatalyst coating composition may be coated on the surface of the substrate a plurality of times. Alternatively, a plurality of different photocatalyst coating compositions may be provided followed by successive coating of the plurality of different photocatalyst coating compositions onto the surface of the substrate. When an identical photocatalyst coating composition is coated a plurality of times, the "coating to form a stacked or multi-layered coating" refers to the so-called "multi-coating" or "recoating." In this case, an even coating can be realized.

[0058] According to another preferred embodiment of

the present invention, a composition composed of a binder and a solvent and substantially free from the photocatalytic metal oxide and the precursor of the photocatalytic metal oxide is first coated followed by coating of a photocatalyst coating composition comprising the photocatalytic metal oxide and/or the precursor of the photocatalytic metal oxide or a photocatalyst coating composition comprising the photocatalytic metal oxide and/or the precursor of the photocatalytic metal oxide and the binder. When satisfactory development of non-crosslinked oxygen is contemplated, preferably, a photocatalyst coating composition is first coated followed by coating of a composition composed of a binder and a solvent to form a stacked or multi-layer coating structure. Fig. 2 is a schematic diagram showing a functional material according to this embodiment. A layer 2a of a photocatalyst coating composition is coated onto a substrate 1, and a layer 4a composed of a binder and a solvent is coated on the layer 2a (Fig. 2 (a)). Upon rapid coating, the photocatalyst coating composition layer 2a is brought to a thin layer 2b which imparts photocatalytic activity to the substrate 1, while the layer 4a is brought to a layer 4b which has non-crosslinked oxygen and contributes to the development of hydrophilic nature. Thus, a functional material 3 having photocatalytic activity is obtained (Fig. 2 (b)).

#### (d) Rapid heating

[0059] The surface of the substrate coated with the photocatalyst coating composition is then subjected to rapid heating. As used herein, the term "rapid heating" means heating for such a period of time that, although heat is evenly spread to the photocatalyst coating composition on the substrate, the temperature of the whole substrate does not yet reach the temperature of the coating on the surface of the substrate. Therefore, preferably, the rapid heating is carried out by intensively applying heat only to the surface of the substrate.

[0060] According to a preferred embodiment of the present invention, the rapid heating is carried out by heating the surface of the substrate to 100 to 800°C, more preferably to 150 to 600°C. Further, as described above, the heating time is such that the temperature of the whole substrate does not yet reach the above temperature. More specifically, the rapid heating time is preferably about 2 to 60 sec, more preferably 5 to 30 sec. Rapidly heating the surface of the substrate to the above temperature can realize the production of a functional material having satisfactory photocatalytic activity with high efficiency. This is particularly because heating to the above temperature range results in the formation of non-crosslinked oxygen with high efficiency which is very advantageous from the viewpoint of the development of hydrophilicity. Further, since the whole substrate does not reach the high temperature, breaking or cracking due to heat shock during temperature rise can be effectively prevented. Further, at the time of cooling,

similar phenomena can be effectively prevented.

[0061] According to a preferred embodiment of the present invention, the heating temperature is kept constant during rapid heating. According to a preferred embodiment of the present invention, the temperature of the atmosphere in which the substrate is placed during rapid heating is preferably 100 to 1000°C.

[0062] According to a preferred embodiment of the present invention, the rapid heating is carried out using heating means of which the heating value per unit area is not less than 120 MJ/m<sup>2</sup>·hr, more preferably not less than 400 MJ/m<sup>2</sup>·hr.

[0063] The rapidly heated substrate is then cooled to provide a final functional material. According to a preferred embodiment of the present invention, the cooling may be rapidly carried out.

#### Apparatus for producing functional material

[0064] According to the present invention, an apparatus suitable for producing the functional material is provided.

[0065] Fig. 3 is an explanatory view of the apparatus for producing a functional material according to the present invention. In the apparatus shown in the drawing, the apparatus according to the present invention is provided continuously from an apparatus for producing a substrate. The apparatus for producing the so-called "earthenware" as the substrate comprises a forming device 5, a grazing device 6, and a firing device 7. The apparatus according to the present invention comprises a device 8 for coating a photocatalyst coating composition, a rapid heating device 9, and a cooling device 10. The apparatus for producing a substrate is provided so as to continue to the apparatus according to the present invention. Further, a carrying device 16 is provided so that the substrate can be continuously carried through within each device and between devices. Therefore, the apparatus for producing a substrate, comprising a substrate forming device 5, a grazing device 6, and a firing device 7 may be properly selected and may have other construction according to the substrate to which the process of the present invention is to be applied. The apparatus according to the present invention is not limited to an apparatus comprising a coating device 8 for coating a photocatalyst coating composition, a rapid heating device 9, and a cooling device 10, and comprises an apparatus, as shown in Fig. 3, which can continuously produce a functional material having photocatalytic activity from the production of a substrate. That is, a construction, wherein an apparatus comprising a coating device 8 for coating a photocatalyst coating composition, a rapid heating device 9, and a cooling device 10 is disposed just behind (downstream of) the apparatus for producing a substrate, also falls within the scope of the present invention.

[0066] A substrate is formed in the forming device 5 shown in the drawing. The substrate is coated with a

grazie by means of the grazing device 6, and then fired in the firing device 7. The substrate, which has been fired in the firing device 7, has still high temperature. According to a preferred embodiment of the present invention, the photocatalyst coating composition is coated onto the substrate when the substrate is still in the state of a certain high temperature.

[0067] The construction of the coating device 8 shown in the drawing may vary depending upon selected coating methods. For example, when spray coating is selected, the coating device comprises a device for spraying a photocatalyst coating composition.

[0068] Fig. 4 is a schematic diagram showing the structure of the rapid heating device 9 shown in Fig. 3. The rapid heating device 9 basically comprises a heating element 21, a heat-resistant material 22 provided so as to cover the heating element 21 and to form a heating space, carrying means 16 for holding a substrate 23, to be heated, within the heating space and carrying the substrate 23 in a direction indicated by an arrow A, a carry-in port 24 for carrying the substrate in the heating space, and a carry-out port 25 for carrying out the substrate from the heating space.

[0069] The heating element 21 is not particularly limited so far as it can rapidly heat the substrate. Heating elements usable herein include electrical heating elements and heating elements which burn a gas or other fuel to generate heat. As described above, preferably, the rapid heating is carried out using heating means of which the heating value per unit area is not less than 120 MJ/m<sup>2</sup>.hr, more preferably not less than 400 MJ/m<sup>2</sup>.hr. Therefore, preferably, the heating element can generate the above heating value. The distance of the surface of the substrate from the heating element may be properly determined so that a satisfactory heating value for rapid heating is applied to the substrate. The distance would be generally about 5 to 300 mm. Therefore, preferably, the heating element is provided so that the distance between the heating element and the substrate is fixed or variable in the above range.

[0070] As described above, preferably, the heating temperature is kept substantially constant during rapid heating. Therefore, preferably, the heating space of the rapid heating device is satisfactorily insulated by an insulating material 22 and undergoes no significant influence of heat loss from the carry-in port 24 and the carry-out port 25. The carry-in port 24 and the carry-out port 25 may be always in released state as shown in Fig. 4. Alternatively, the carry-in port 24 may be constructed so that the port 24 is usually closed while the port 24 is opened when the substrate is carried in the rapid heating device. Likewise, the carry-out port 25 may be constructed so that the port 25 is usually closed while the port 25 is opened when the substrate is carried out from the rapid heating device. The length of the region where the temperature for rapid heating is kept substantially constant may be properly determined. The length would be generally 5 cm to 30 m.

[0071] The construction of the carrying device 16 is not particularly limited so far as the device can hold the substrate within the heating space and carries through the heating space. The carrying device 16 is preferably a belt conveyor or a roller conveyor. According to a preferred embodiment of the present invention, in order to attain good thermal conduction within the heating space, the carrying device 16 is constructed so that the heating space is not excessively thermally partitioned. For example, the carrying means is preferably a belt conveyor of a heat-resistant porous belt having a percentage surface opening of not less than 20% or a roller conveyor of a group of heat-resistant rollers. Further, according to a preferred embodiment of the present invention, the carrying means is a belt conveyor of a heat-resistant net having a mesh size of 50 mm x 40 mm or a roller conveyor of a group of continuous heat-resistant rollers having a pitch of 1 to 300 mm.

[0072] The surface of the rapidly heated substrate is cooled by the cooling device 10 to room temperature. In this device, the substrate is placed in an atmosphere of room temperature and the surface of it is cooled to room temperature. So far as the temperature of the surface of the substrate can be decreased to room temperature, this cooling device may be constructed so that the substrate simply comes into contact with air of room temperature to lower the temperature of the surface of the substrate. Alternatively the device may be constructed so that air of room temperature or air having a temperature slightly above or below room temperature is forcibly blown against the substrate to lower the temperature of the surface of the substrate. In this connection, it should be noted that rapid cooling has a fear of cracking or the like being created on the surface of the functional material. Therefore, preferably, the cooling is carried out at a highest possible rate with caution so as not to create cracking or other unfavorable phenomenon.

[0073] Fig. 5 shows an apparatus provided with a preheating device for preheating the surface of the substrate before coating of the photocatalyst coating composition. The preheating device can heat the surface of the substrate and raise the temperature of the surface of the substrate to a temperature high enough for evenly coating the photocatalyst coating composition. In the apparatus shown in Fig. 5, a preheating device 11 is provided before the coating device 8. As described above, preferably, the surface of the substrate is heated by this preheating device to a temperature of 20 to 400°C. It is a matter of course that an apparatus, shown in Fig. 3, comprising a substrate molding device 5, a grazing device 6, and a firing device 7 may be connected upstream of the preheating device 11. In this connection, however, since the substrate heated in the firing device 7 still has high temperature, when the functional material having photocatalytic activity is produced continuously from the production of a substrate, the provision of this preheating device is generally unnecessary. Therefore, the preheating device would be generally necessary when the

substrate has been separately produced and hence does not have satisfactory temperature.

[0074] Further, in the apparatus shown in Fig. 5, a drying device 12 for drying the substrate coated with the photocatalyst coating composition by means of the coating device 8 is provided before the rapid heating device 9. This drying device 12 comprises air blowing means or heating means to remove excess water or solvent component from the surface of the substrate. In the apparatus shown in Fig. 5, the rapid heating device 9 and the cooling device 10 may be identical respectively to those shown in Fig. 3.

## EXAMPLES

### Example 1

#### (a) Preparation of photocatalyst coating composition

[0075] At the outset, a titanium sol (tradename: STS-21, manufactured by Ishihara Sangyo Kaisha Ltd.), a silica sol (tradename: Snowtex S, manufactured by Nissan Chemical Industry Ltd.), and lithium silicate (tradename: Lithium Silicate 35, manufactured by The Nippon Chemical Industrial Co., Ltd.) were mixed together. A 1% aqueous silver nitrate solution in an amount of 1 part by weight based on 1 part by weight of titanium oxide and a 0.3% aqueous copper acetate solution in an amount of 2 parts by weight based on 1 part by weight of titanium oxide were added to the mixture, followed by irradiation with ultraviolet light (intensity of ultraviolet light about 1 mW/cm<sup>2</sup>) for 4 hr, during which time the solution was stirred so as to satisfactorily irradiate the solution with ultraviolet light. Thus, a mixed sol as a photocatalyst coating composition was prepared which was composed of: a titanium sol with silver and copper being supported on a titanium oxide photocatalyst; a silica sol; and a lithium silicate. The final concentration in the mixed sol was 0.2% by weight for the titanium sol (solid content 0.1%), 0.3% by weight for the silica sol, and 0.4% by weight for lithium silicate.

#### (b) Preparation of substrate

[0076] In an apparatus shown in Fig. 3, a starting material for ceramic ware was pressed in a forming device 5 to prepare a body. A glaze was coated onto the surface of the body in a glazing device 6. The coated body was passed through a roller hearth kiln as a firing device 7 kept at a firing temperature of 1150°C over a period of 40 min to perform firing. Thus, a tile was obtained.

#### (c) Production of functional material

[0077] In an apparatus shown in Fig. 3, when the temperature of the tile became 150°C at the outlet of the roller hearth kiln, the photocatalyst coating composition prepared above was spray coated by means of a coating

device 8 onto the surface of the tile. The coverage of the photocatalyst coating composition was 15 g/m<sup>2</sup>. Since the temperature of the tile was as high as 150°C, excess water was instantaneously evaporated. As a result, only solid matter was evenly stacked on the surface of the tile to form an about 0.1 μm-thick thin layer.

[0078] The tile was then carried in a furnace as a rapid heating device provided continuously from the coating device 8. The furnace had heating elements densely arrayed on the upper part of the interior thereof. The temperature of the atmosphere in the furnace was about 800 to 1000°C, the heating value per unit area within the furnace was about 1600 MJ/m<sup>2</sup>-hr, and the heating area was 30 cm x 150 cm. The time of residence of the tile within the furnace was about 30 sec, and the time for which the tile had been placed under the heating elements was about 10 sec. The rapid heating permitted the thin layer formed on the surface of the tile to be completely fixed onto the surface of the tile.

[0079] The surface of the tile carried out from the furnace had a temperature increased to 300 to 350°C. Subsequently, the tile was introduced into a cooling device where the tile was sprayed with cold air blown from above and below the tile. The tile was cooled to 100-150°C during the period of time for which the tile was traveled by 3 m through the cooling device.

[0080] The tile as a functional material thus obtained had photocatalytic activity and high decomposition activities, such as antimicrobial activity, antifouling activity, and deodorant activity, and further was hydrophilic. The thin layer formed on the surface of the tile was a strong layer which had a strength (hardness) of not less than 4 in terms of Mohs hardness and possessed excellent abrasion resistance and chemical resistance.

[0081] The heat of wetting of the thin layer by water was determined and found to be as high as 500 erg/cm<sup>2</sup>, suggesting that the thin layer had satisfactory hydrophilicity. The heat of wetting is regarded as a measure of wettability by a solvent, and higher heat of wetting means that the wettability by the solvent is high.

### Example 2

#### (a) Preparation of photocatalyst coating composition

[0082] A photocatalyst coating composition was prepared in the same manner as in Example 1, except that 1 part by weight of a 3% aqueous copper acetate solution was used instead of 1 part by weight of the 1% aqueous silver nitrate solution and 2 parts by weight of the 0.3% aqueous copper acetate solution.

#### (b) Preparation of substrate

[0083] A large tile (0.9 m x 1.8 m) was prepared in the same manner as in Example 1. Specifically, a starting material for ceramic ware was extruded by means of a forming device 5 in the apparatus shown in Fig. 3 to pre-

pare a body. A glaze was coated onto the surface of the body by means of a glazing device 6. The coated body was passed through a roller hearth kiln as a firing device 7 kept at a firing temperature of 1150°C over a period of 3 hr to perform sintering. Thus, a large tile was obtained.

#### (c) Production of functional material

[0084] In an apparatus shown in Fig. 3, when the temperature of the tile became 80 °C, the photocatalyst coating composition as used in Example 1 was spray coated onto the surface of the tile by means of a coating device 8. The coverage of the photocatalyst coating composition was 15 g/m<sup>2</sup>. Since the temperature of the tile was as high as 80°C, excess water was instantaneously evaporated. As a result, only solid matter was evenly stacked on the surface of the tile to form an about 0.1 μm-thick thin layer.

[0085] The tile was then carried in a furnace as a rapid heating device continuously provided from the coating device 8. The furnace had heating elements densely arrayed on the upper part of the interior thereof. The temperature of the atmosphere in the furnace was about 800 to 1000°C, the heating value per unit area within the furnace was about 1600 MJ/m<sup>2</sup>-hr, and the heating area was 1.5 m x 28 m. The time of residence of the tile within the furnace was about 60 sec, and the time for which the tile had been placed under the heating elements was about 50 sec. The rapid heating permitted the thin layer formed on the substrate to be completely fixed onto the surface of the tile.

[0086] The surface of the tile carried out from the furnace had a temperature increased to 200 to 250°C. Subsequently, the tile was introduced into a cooling device where the tile was sprayed with water. In the cooling device, the tile was cooled to 100-150°C during the period of time for which the tile was traveled by 10 m through the cooling device.

[0087] The tile as a functional material thus obtained had photocatalytic activity and high decomposition activities, such as antimicrobial activity, antifouling activity, and deodorant activity, and further was hydrophilic. The thin layer formed on the surface of the tile was a strong layer which had a strength (hardness) of not less than 4 in terms of Mohs hardness and possessed excellent abrasion resistance and chemical resistance.

#### Example 3

##### (a) Preparation of photocatalyst coating composition

[0088] A titanium alkoxide (titanium tetraisopropoxide) and tetraethyl orthosilicate were diluted with isopropyl alcohol to prepare a photocatalyst coating composition having a titanium alkoxide concentration of 5% by weight and a tetraethyl orthosilicate concentration of 1% by weight.

##### (b) Substrate

[0089] A glass plate having a size of 1 m x 1 m was provided as a substrate.

##### (c) Production of functional material

[0090] A functional material was produced using the same apparatus as shown in Fig. 5, except that, instead of provision of a pair of the coating device 8 and the drying device 12, the coating device 8 and the drying device 12 were alternately provided in three pairs. At the outset, the glass plate was heated to a surface temperature of 40°C in a preheating device 11 kept at a temperature of 40°C. The photocatalyst coating composition was spray coated on the surface of the glass plate. The coverage was 5 g/m<sup>2</sup>. Since the temperature of the glass substrate is as low as 40°C, the water and the alcohol are less likely to be evaporated, for this reason, after coating of the photocatalyst coating composition, the coating was dried at 100°C. The coating followed by drying was repeated three times. This permitted only solid matter to be evenly stacked on the surface of the glass plate to form an about 0.1 μm-thick thin layer.

[0091] Next, the glass plate with a thin layer formed thereon was carried in a furnace as a rapid heating device 9 provided continuously from the last drying device 12. The furnace had heating elements densely arrayed on the upper part of the interior thereof. The temperature of the atmosphere in the furnace was about 550°C. The time of residence of the glass plate within the furnace was about 2 sec. The rapid heating permitted the thin layer formed on the glass substrate to be completely fixed onto the surface of the glass plate.

[0092] The surface of the glass plate carried out from the furnace had a temperature increased to 250 to 350°C. Subsequently, the glass plate with a thin layer fixed thereon was introduced into a cooling device where air was blown against the glass plate. In the cooling device, the glass plate was cooled to 50-150°C during the period of time for which the glass plate was traveled by 3 m through the cooling device.

[0093] The functional material thus obtained had high surface smoothness, photocatalytic activity, high degradation activity, and high hydrophilicity.

[0094] The thin layer formed on the surface of the glass plate was a strong layer which had a strength (Mohs hardness) of not less than 4 and possessed excellent abrasion resistance and chemical resistance.

#### Example 4

##### (a) Preparation of photocatalyst coating composition

[0095] The same photocatalyst coating composition as used in Example 1 was provided.

## (b) Substrate

[0096] An inorganic decorative plate having thereon an acrylated urethane coating and, further, a fluororesin coating was provided as a substrate.

## (c) Production of functional material

[0097] A functional material was produced using an apparatus shown in Fig. 5. The surface of the substrate was heated to 60°C in the preheating device 11 set at a temperature of 60°C. The photocatalyst coating composition was spray coated on the surface of the substrate. The coverage was 20 g/m<sup>2</sup>.

[0098] The coated substrate was then carried in a rapid heating device 9 provided continuously from the drying device 12. The rapid heating device 9 was a roller hearth kiln (RHK) (the temperature of the atmosphere 250°C). The substrate with a coating formed thereon was passed through RHK over a period of about 45 sec to perform rapid heating. The rapid heating permitted the photocatalyst coating composition to be completely fixed onto the surface of the inorganic decorative plate as the substrate.

[0099] The functional material having photocatalytic activity thus obtained had high surface smoothness, decomposition activity and oil repellency. The thin layer formed on the substrate was a strong layer possessing excellent abrasion resistance and chemical resistance.

Example 5

## (a) Preparation of photocatalyst coating composition

[0100] At the outset, a titanium sol (STS-21), a silica sol (tradename: Snowtex O, manufactured by Nissan Chemical Industry Ltd.), lithium silicate (tradename: Lithium Silicate 35, manufactured by Nissan Chemical Industry Ltd.), and a surfactant (Kao Emulgen 707) were mixed together. A 1% aqueous silver nitrate solution in an amount of 1 part by weight based on 1 part by weight of titanium oxide and a 0.3% aqueous copper acetate solution in an amount of 2 parts by weight based on 1 part by weight of titanium oxide were added to the mixture, followed by irradiation with ultraviolet light (intensity of ultraviolet light about 1 mW/cm<sup>2</sup>) for 4 hr, during which time the solution was stirred so as to satisfactorily irradiate the solution with ultraviolet light. Thus, a mixed sol as a photocatalyst coating composition was prepared which was composed of: a titanium sol with silver and copper being supported on a titanium oxide photocatalyst; a silica sol; lithium silicate; and a surfactant. The final concentration in the mixed sol was 0.1% by weight for the titanium sol, 0.1% by weight for the silica sol, 0.5% by weight for lithium silicate, and 0.001% by weight for the surfactant.

## (b) Substrate

[0101] Western tableware was provided as a substrate.

## (c) Production of functional material

[0102] A functional material was produced using an apparatus shown in Fig. 5. At the outset, the tableware was heated to a surface temperature of 100°C in a preheating device 11 set at a temperature of 100°C. The photocatalyst coating composition was spray coated on the surface of the tableware. The coverage was 40 g/m<sup>2</sup>. Since the temperature of the tableware was as high as 100°C, water was instantaneously evaporated. As a result, only solid matter was evenly stacked on the surface of the tableware to form an about 0.4 μm-thick thin layer.

[0103] The tableware with a thin layer formed thereon was then carried in a furnace as a rapid heating device 9 continuously provided from the drying device 12. The furnace had heating elements densely arrayed on the upper part of the interior thereof. The temperature of the atmosphere in the furnace was about 800 to 1000°C, the heating value per unit area within the furnace was about 1600 MJ/m<sup>2</sup>-hr, and the heating area was 30 cm x 150 cm. The time of residence of the tableware within the furnace was about 10 sec. The rapid heating permitted the thin layer formed on the surface of the tableware to be completely fixed onto the surface of the tableware.

[0104] The surface of the tableware carried out from the furnace had a temperature increased to 250 to 300°C. Subsequently, the tableware was introduced into a cooling device where the tableware was subjected to air blast cooling. The tableware was cooled to 50-150°C during the period of time for which the tableware was traveled by 3 m through the cooling device.

[0105] The tableware with a thin layer formed thereon thus obtained as a functional material had photocatalytic activity and excellent antimicrobial activity. A salad oil was deposited on the functional material and then washed in water. As a result, the salad oil deposited on the surface thereof could be easily removed by washing in water alone.

[0106] The thin layer formed on the surface of the tableware was a strong layer which had a strength (hardness) of not less than 4 in terms of Mohs hardness and possessed excellent abrasion resistance and chemical resistance.

Example 6

[0107] A functional material was produced using an apparatus shown in Fig. 5. At the outset, a tile was heated to a surface temperature of 100°C in a preheating device 11 set at a temperature of 100°C. A titanium chelate (0.05%) as a photocatalyst coating composition was then spray coated on the surface of the tile as the



substrate. Water was immediately evaporated, and solid matter was fixed onto the surface of the tile to form an about 0.2  $\mu\text{m}$ -thick thin layer.

[0108] The tile with a thin layer formed thereon was then carried in a furnace as a rapid heating device continuously provided from the drying device 12. The furnace had heating elements densely arrayed on the upper part of the interior thereof. The temperature of the atmosphere in the furnace was about 800 to 1000°C, the heating value per unit area within the furnace was about 1600 MJ/m<sup>2</sup>-hr, and the heating area was 30 cm x 150 cm. The time of residence of the tile within the furnace was about 10 sec. The rapid heating permitted the thin layer formed on the tile to be completely fixed onto the surface of the tile.

[0109] The surface of the tile carried out from the furnace had a temperature increased to 250 to 300°C. Subsequently, the tile was introduced into a cooling device where the tile was subjected to air blast cooling. The tile was cooled to 50-150°C during the period of time for which the tile was traveled by 3 m through the cooling device.

[0110] The tile with a thin layer formed thereon thus obtained as a functional material had photocatalytic activity and excellent hydrophilicity and antimicrobial activity.

[0111] The thin layer formed on the surface of the tile was a strong layer which had a strength (hardness) of not less than 4 in terms of Mohs hardness and possessed excellent abrasion resistance and chemical resistance.

#### Example 7

[0112] A functional material was produced using an apparatus shown in Fig. 5. A tile was heated to a surface temperature of 100 to 300°C in a preheating device. A water-soluble coating liquid prepared by mixing a predetermined amount of a titanium oxide sol, a predetermined amount of an alkali silicate, and a predetermined amount of an alumina sol together and adjusting the mixture to a TiO<sub>2</sub> concentration of 0.2%, an SiO<sub>2</sub> concentration of 0.1%, an Li<sub>2</sub>O concentration of 0.008%, an Na<sub>2</sub>O concentration of 0.012%, a B<sub>2</sub>O<sub>3</sub> concentration of 0.0015%, and an Al<sub>2</sub>O<sub>3</sub> concentration of 0.005% was spray coated at a coverage of 2 to 3  $\mu\text{g}$  per cm<sup>2</sup> of the tile surface. Water was immediately evaporated, and solid matter was fixed onto the surface of the tile. Next, the tile with solid matter fixed thereon was fired in the rapid heating device 9 provided continuously from the drying device 12 under conditions of in-furnace temperature about 850°C, heating value 1200 MJ/m<sup>2</sup>-hr, and heating area 0.6 m<sup>2</sup>. In this case, the highest temperature of the surface of the tile was 480°C. The time of residence of the tile within the furnace was about 15 sec. As a result, a thin layer was formed on the surface of the tile. The photocatalytic activity of the functional material sample thus obtained was determined as follows.

A 1% silver nitrate solution was coated onto the surface of the sample. The coated sample was allowed to stand under a BLB lamp for 5 min. The color difference ( $\Delta E$ ) was then measured and found to be about 18. Further, the sample was allowed to stand under a BLB lamp for 24 hr. The contact angle of the sample with water was then measured and found to be about 5 degrees.

#### Example 8

[0113] A functional material was produced using an apparatus shown in Fig. 5. A tile was heated to a surface temperature of 200°C in a preheating device 11. An aqueous solution prepared by mixing a copper-doped titanium oxide sol and an alkali silicate together and adjusting the mixture to a TiO<sub>2</sub> concentration of 0.08%, a CuO concentration of 0.004%, an SiO<sub>2</sub> concentration of 0.3%, an Li<sub>2</sub>O concentration of 0.025%, an Na<sub>2</sub>O concentration of 0.04%, and a B<sub>2</sub>O<sub>3</sub> concentration of 0.005% was spray coated at a coverage of 2 to 3  $\mu\text{g}$  per cm<sup>2</sup> of the substrate surface. Water was immediately evaporated, and solid matter was fixed onto the surface of the tile. Next, the tile with solid matter fixed thereon was fired in the rapid heating device 9 provided continuously from the drying device 12 under conditions of in-furnace temperature about 750°C, heating value 1200 MJ/m<sup>2</sup>-hr, and heating area 0.6 m<sup>2</sup>. In this case, the highest temperature of the surface of the tile as the substrate during firing was 350°C. The time of residence of the tile within the furnace was about 10 sec. As a result, a thin layer was formed on the surface of the tile. The photocatalytic activity of the functional material sample thus obtained was determined as follows. A 1% silver nitrate solution was coated onto the surface of the sample. The coated sample was allowed to stand under a BLB lamp for 5 min. The color difference ( $\Delta E$ ) was then measured and found to be about 18. Further, the surface of the sample had high antimicrobial activity.

#### Claims

1. A process for producing a functional material having photocatalytic activity, comprising the steps of: coating a photocatalyst coating composition comprising a photocatalytic metal oxide and/or a precursor of the photocatalytic metal oxide onto the surface of a substrate; and rapidly heating the surface of the coated substrate to fix the photocatalytic metal oxide onto the surface of the substrate.
2. The process according to claim 1, wherein the rapid heating is carried out by heating the surface of the substrate to 100 to 800°C.
3. The process according to claim 2, wherein the rapid heating is carried out by heating the surface of the

substrate to 150 to 600°C.

4. The process according to any one of claims 1 to 3, wherein, during the rapid heating, the substrate is placed in an atmosphere of 100 to 1000°C.
5. The process according to any one of claims 1 to 4, wherein the rapid heating is carried out for 2 to 60 sec.
6. The process according to any one of claims 1 to 5, wherein, during the rapid heating, the heating temperature is kept substantially constant.
7. The process according to any one of claims 1 to 6, wherein the surface of the substrate is preheated before coating of the photocatalyst coating composition.
8. The process according to any one of claims 1 to 7, wherein the preheating is carried out by heating the surface of the substrate to 20 to 400°C.
9. The process according to any one of claims 1 to 8, wherein the rapid heating is carried out by intensively supplying heat energy only to the surface of the substrate.
10. The process according to any one of claims 1 to 9, wherein the rapid heating is carried out by heating means of which the heating value per unit area is not less than 120 MJ/m<sup>2</sup>.hr.
11. The process according to any one of claims 1 to 10, wherein the substrate coated with the photocatalyst coating composition is dried before the rapid heating.
12. The process according to any one of claims 1 to 11, wherein the surface of the rapidly heated substrate is then rapidly cooled.
13. The process according to any one of claims 1 to 12, wherein the photocatalytic metal oxide is selected from the group consisting of TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, SrTiO<sub>3</sub>, WO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub>.
14. The process according to any one of claims 1 to 13, wherein the precursor of the photocatalytic metal oxide is a compound which contains at least one metal selected from the group consisting of titanium, zinc, tin, strontium, tungsten, bismuth, iron, and vanadium and, upon the rapid heating, is converted to the photocatalytic metal oxide.
15. The process according to any one of claims 1 to 14, wherein the photocatalyst coating composition further comprises a binder.
16. The process according to claim 15, wherein the binder comprises: at least one member selected from the group consisting of inorganic oxide particles, silicone resin film precursors capable of forming silicone resin films, and silica film precursors capable of forming silica films; and a solvent.
17. The process according to claim 15, wherein the binder comprises:  
a member selected from the group consisting of silicon, aluminum, potassium, lithium, sodium, cesium, calcium, magnesium, titanium, phosphorus, boron, zirconium, rubidium, francium, yttrium, hafnium, lanthanides, and compounds of said elements; and  
an alkali silicate represented by formula Me<sub>2</sub>O·nSiO<sub>2</sub> wherein Me represents an alkali metal.
18. The process according to any one of claims 1 to 17, wherein an identical photocatalyst coating composition is coated a plurality of times on the surface of the substrate to form a stacked or multi-layered coating, or alternatively, a plurality of different photocatalyst coating compositions are provided followed by successive coating of the plurality of photocatalytic coating compositions onto the surface of the substrate to form a stacked or multi-layered coating.
19. The process according to any one of claims 1 to 18, which comprises the steps of: providing at least one coating composition comprising a binder and substantially free from the photocatalytic metal oxide and the precursor of the photocatalytic metal oxide and a photocatalyst coating composition comprising the photocatalytic metal oxide and/or the precursor of the photocatalytic metal oxide or a photocatalyst coating composition comprising the photocatalytic metal oxide and/or the precursor of the photocatalytic metal oxide and the binder;  
coating them onto the surface of the substrate to form a multi-layered coating; and  
then rapidly heating the assembly.
20. The process according to any one of claims 1 to 19, wherein the photocatalyst coating composition further comprises a metal and/or a metal oxide selected from silver, copper, zinc, metals of the platinum group, and oxides of said metals.
21. The process according to claim 20, wherein the metal and the metal oxide are present, in a supported state, on the surface of the photocatalytic metal oxide.

22. The process according to claim 21, wherein the metal and the metal oxide have been supported on the surface of the photocatalytic metal oxide by photo-reduction fixation using ultraviolet light irradiation.
23. The process according to any one of claims 1 to 22, wherein the concentration of the photocatalytic metal oxide and/or the precursor of the photocatalytic metal oxide in the photocatalyst coating composition is 0.001 to 35% by weight on a solid basis.
24. The process according to any one of claims 1 to 23, wherein the photocatalyst coating composition contains the binder in an amount of 0.001 to 100 parts by weight based on one part by weight of the photocatalytic metal oxide and the precursor of the photocatalyst metal oxide.
25. The process according to any one of claims 1 to 24, wherein the photocatalyst coating composition contains the binder in an amount of 0.1 to 5 parts by weight based on one part by weight of the photocatalytic metal oxide and the precursor of the photocatalytic metal oxide.
26. The process according to any one of claims 1 to 25, wherein the substrate is made of a metal, an inorganic material, an organic material, or a composite material thereof.
27. The process according to any one of claims 1 to 26, wherein the functional material having photocatalytic activity is an interior or exterior material.
28. The process according to any one of claims 1 to 26, wherein the functional material having photocatalytic activity is a tile, a sanitary ware, a table ware, a calcium silicate board, a building material, a ceramic substrate, a semiconductor material, an insulator, a glass, a mirror.
29. An apparatus for producing a functional material having photocatalytic activity, said apparatus comprising at least
- coating means for coating a photocatalyst coating composition comprising a photocatalytic metal oxide and/or a precursor of the photocatalytic metal oxide onto the surface of a substrate and
- heating means for rapidly heating the surface of the coated substrate to fix the photocatalytic metal oxide onto the surface of the substrate.
30. The apparatus according to claim 29, which carries out the method according to any one of claims 1 to 28.

31. The apparatus according to claim 30 or 31, wherein the heating value per unit area of the rapid heating means is not less than 120 MJ/m<sup>2</sup>.hr.
32. The apparatus according to any one of claims 29 to 31, wherein the heating means can maintain the heating temperature at a substantially constant value.
33. The apparatus according to any one of claims 29 to 32, wherein the rapid heating means maintains the heating temperature at a substantially constant value over a zone length of 5 cm to 30 m.
34. The apparatus according to any one of claims 29 to 33, wherein the rapid heating means comprises at least a heating element, a heat-resistant material which covers the heating element while forming a given heating space, holding means for holding the substrate within the heating space, a carry-in port for carrying the substrate in the heating space, and a carry-out port for carrying out the substrate from the heating space.
35. The apparatus according to any one of claims 29 to 34, wherein the heating element is provided so that the distance between the heating element and the surface of the substrate is 5 to 300 mm with the distance being fixed or variable.
36. The apparatus according to any one of claims 29 to 35, which further comprises preheating means for preheating the surface of the substrate before coating the photocatalyst coating composition.
37. The apparatus according to any one of claims 29 to 35, which further comprises drying means for drying the substrate coated with the photocatalyst coating composition by the coating means.
38. The apparatus according to any one of claims 29 to 37, which further comprises cooling means for rapidly cooling the surface of the substrate heated by the heating means.
39. The apparatus according to any one of claims 29 to 38, which comprises carrying means for continuously moving and carrying the substrate within the apparatus.
40. The apparatus according to any one of claims 29 to 39, wherein the rapid heating means is disposed immediately downstream of the coating means.
41. The apparatus according to any one of claims 29 to 40, which is disposed immediately downstream of an apparatus for producing the substrate.

42. The apparatus according to any one of claims 29 to 41, wherein the carrying means is a belt conveyor or a roller conveyor.
43. The apparatus according to claim 42, wherein the carrying means is a belt conveyor of a heat-resistant belt having a percentage surface opening of not less than 20% or a roller conveyor of a group of rollers.
44. The apparatus according to claim 42, wherein the belt conveyor comprises a heat-resistant net having a mesh size up to 50 mm x 50 mm.
45. The apparatus according to claim 42, wherein the roller conveyor comprises continuous heat-resistant rollers having a pitch of 1 to 300 mm.
46. A functional material having photocatalytic activity, produced by the method according to any one of claims 1 to 28 or the apparatus according to any one of claims 29 to 45.
47. A photocatalyst coating composition consisting essentially of a photocatalytic metal oxide and/or a precursor of the photocatalytic metal oxide and an alkali silicate and/or a precursor of the alkali silicate.
48. The photocatalyst coating composition according to claim 47, which further comprises a metal and/or a metal oxide.
49. The photocatalyst coating composition according to claim 48, wherein the metal is in the form of particles of at least one member selected from the group consisting of copper, silver, platinum, cobalt, iron, nickel, gold, zinc, chromium, manganese, and molybdenum and the metal oxide is in the form of particles of at least one member selected from the group consisting of  $\text{Cu}_2\text{O}$  and  $\text{Ag}_2\text{O}$ .
50. The photocatalyst coating composition according to claim 48, wherein the metal oxide is an oxide of at least one metal selected from the group consisting of silicon, aluminum, potassium, lithium, sodium, cesium, rubidium, and francium.
51. The photocatalyst coating composition according to claim 48 or 49, wherein the metal and/or the metal oxide are previously supported on the photocatalytic metal oxide and/or the precursor of the photocatalytic metal oxide.
52. The photocatalyst coating composition according to claim 51, wherein the metal and/or the metal oxide have been supported by photoreduction.
53. A hydrophilic functional material comprising: a substrate; and a layer provided on the surface of the substrate, the layer consisting essentially of a photocatalytic metal oxide and an alkali silicate.
54. The hydrophilic functional material according to claim 53, wherein the layer further comprises a metal and/or a metal oxide.
55. The hydrophilic functional material according to claim 54, wherein the metal is in the form of particles of at least one member selected from the group consisting of copper, silver, platinum, cobalt, iron, nickel, gold, zinc, chromium, manganese, and molybdenum and the metal oxide is in the form of particles of at least one member selected from the group consisting of  $\text{Cu}_2\text{O}$  and  $\text{Ag}_2\text{O}$ .
56. The hydrophilic functional material according to claim 54, wherein the metal oxide is an oxide of at least one metal selected from the group consisting of silicon, aluminum, potassium, lithium, sodium, cesium, rubidium, and francium.
57. The hydrophilic functional material according to claim 54 or 55, wherein the metal and/or the metal oxide have been previously supported on the photocatalytic metal.
58. The hydrophilic functional material according to claim 57, wherein the metal and/or the metal oxide have been supported by photoreduction.

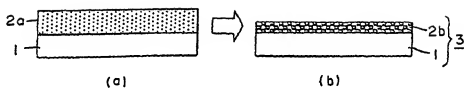


FIG. 1

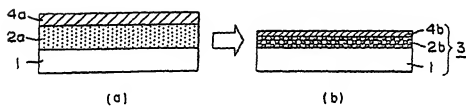


FIG. 2

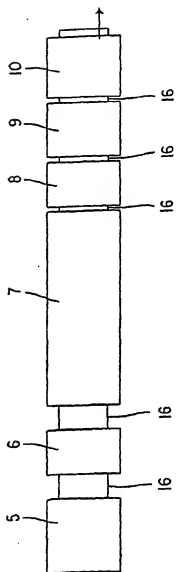


FIG. 3

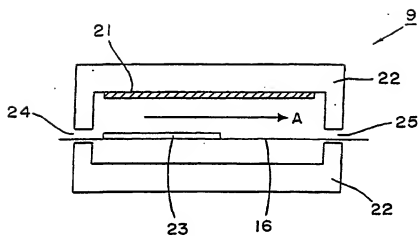


FIG. 4

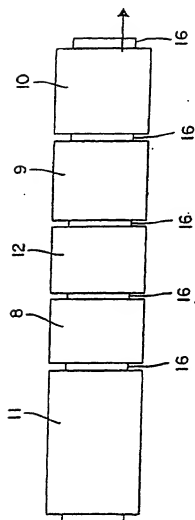


FIG. 5



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/04126

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.<sup>1</sup> B01J35/02, C09D1/00, 5/00, B05D5/00, 7/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>1</sup> B01J35/02, C09D1/00, 5/00, B05D5/00, 7/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999  
Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Kelsai Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 10-180118, A (Sumitomo Metal Industries, Ltd.), 7 July, 1998 (07. 07. 98), Claims ; Par. Nos. [0020] to [0032] ; Examples (Family: none)	1-6, 9, 10, 12-14, 18, 26-35, 38-42, 46
Y		7, 8, 11, 15-17, 19-25, 36, 37, 42-45
Y	JP, 10-1879, A (Komatsu Seiren Co., Ltd.), 6 January, 1998 (06. 01. 98), Claims ; Par. Nos. [0001], [0024], [0025] ; Examples (Family: none)	11, 15-17, 19, 23-25, 37
Y	JP, 9-40872, A (Nippon Kayaku Co., Ltd.), 10 February, 1997 (10. 02. 97), Claims ; Par. Nos. [0015], [0016] ; Examples (Family: none)	7, 8, 36

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search  
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## INTERNATIONAL SEARCH REPORT

 International application No.  
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 8-131841, A (TOTO Ltd.), 28 May, 1996 (28. 05. 96), Claims ; Par. No. [0009] (Family: none)	20-22, 48, 49, 51, 52, 54, 55, 57, 58
Y	Microfilm of the specification and drawings annexed to the request of Japanese Utility Model Application No. 1-131865 (Laid-open No. 3-72297) (Akira Itou), 22 July, 1991 (22. 07. 91), Claims (Family: none)	42-45
X	JP, 8-318166, A (Director General, Agency of Industrial Science and Technology), 3 December, 1996 (03. 12. 96), Full text & US, 5658841, A	47, 53
Y		48-52, 54-58
Y	JP, 9-56792, A (Mitsubishi Paper Mills Ltd.), 4 March, 1997 (04. 03. 97), Claims (Family: none)	50, 56

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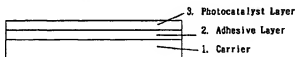
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**(54) PHOTOCATALYST-CARRYING STRUCTURE AND PHOTOCATALYST COATING MATERIAL**

(57) The present invention provides a photocatalyst-carrying structure which has a structure, wherein an adhesive layer is provided in between a photocatalyst layer and a substrate, the adhesive layer is composed of silicon-modified resin, polysiloxane-containing resin or colloidal silica-containing resin, and for forming the photocatalyst layer a composition comprising a metal oxide gel or a metal hydroxide gel and a photocatalyst is used. Further, the present invention also provides a photocatalyst coating agent for producing a photocatalyst-carrying structure which contains silicon compound, at least one metal oxide sol or metal hydroxide sol, and at least one photocatalyst powder or sol.

Fig. 1



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## Description

## Field of the Invention

[0001] The present invention is related to a structure carrying a photocatalyst which is useful for antifouling, cleaning water, deodorization, pasteurization, a treatment of waste water, decomposition of water, a control of algae growth and various chemical reactions.

## Background Art

[0002] Titanium dioxide, which is n-type semiconductor, has been known as a photocatalyst that activates various chemical reactions with ultraviolet radiation energy, such as chemical reactions resulted in during a process of decomposition of water, deodorization, pasteurization, cleaning of water, a treatment of waste water or the like. It is said that the catalytic activity of a photocatalyst can be generally high when it is used either in powder form or in a form of suspension in a solvent, however, in many cases, such photocatalyst is practically obliged to be used in a form being carried on a certain substrate. For utilizing ultraviolet radiation energy from light efficiently, it is advantageous to make a substrate into a shape like a paper or a sheet, which can secure the wider light irradiation area, moreover, it is further advantageous to make the surface of the substrate into a porous structure in order to increase contacting area of the substrate with a reactant with which an objective chemical reaction is desired to be proceeded in the presence of a photocatalyst.

[0003] Various substrates which comprise a photocatalyst have been proposed in the past. For example, (A) a light transmissible material, such as cellulose nitrate, glass, poly(vinyl chloride), plastics, nylon, methacrylic resin and polypropylene, is disclosed in Japanese Patent Laid-opened No. Sho 62-66861, (B) polypropylene fibers and ceramics are disclosed in Japanese Patent Laid-opened No. Hei 2-68190, and (C) glass, ceramics, nylon, acryl and polyester resins are disclosed in Japanese Patent Laid-opened No. Hei 5-309267.

[0004] However, among the materials as disclosed above, it is reported that the one comprising an organic material as its main component has the disadvantage that the organic material can be decomposed and deteriorated due to catalytic reaction caused by a photocatalyst contained in the said material, and the durability thereof has therefore been problematic (see Fumiaki Otani & Kobunsi Kako No. 42, vol. 5, page 18 (1993); "Titanium dioxide", by Manabu Kiyono, published by Gihodo, page 165).

[0005] Further, even though the substrate is composed of an inorganic material, such as glass and ceramics, there must be some problems in the durability property of the substrate, such that, if an organic polymer resin is used as an adhesive for carrying a photocatalyst on the substrate, the photocatalytic activity may be lowered due to coverage of the surface of photocatalyst particles with such resin, and that the photocatalyst may be exfoliated from the substrate due to the cause of decomposition and deterioration of said organic polymer resin by virtue of its photocatalytic activity.

[0006] In order to avoid having such problems as described above, a method called spattering method whereby any organic materials do not remain (Japanese Patent Laid-opened No. Sho 60-044053), a method to coat and bake an organic titanate (Japanese Patent Laid-opened No. Sho 60-118236), a method to spray and bake titania sol (Japanese Patent Laid-opened No. Hei 5-253544), and the others have been employed, in case that the substrate used is an inorganic heat-resistant material.

[0007] However, these methods have a problem that they require a process of baking the substrate at a high temperature in order to obtain production and crystallization of photocatalyst particles over the substrate and adhesive property with the substrate, and therefore, it is difficult to carry photocatalyst over a wide area and the production according to these methods requires very high cost.

[0008] Whereas, for carrying a photocatalyst onto a glass fiber paper, a method to use a metal oxide sol as an adhesive has been proposed (see Japanese Patent Laid-opened No. Hei 5-309267).

[0009] However, the adhesive property of a metal oxide sol, such as silica sol, is very weak because it is derived from van der Waals force (see Fine Ceramics, vol. 1, page 216-223. 1980) so that the binding strength and durability of the adhesive were insufficient. Further, the method additionally requires a process of baking at a high temperature, and therefore, it was not applicable for all types of substrates including commonly used types of resins which are easily decomposed by heating.

[0010] In an example wherein a metal oxide, such as silica gel and clay mineral, in a sol state carrying photocatalyst powder thereon, there is a report that the photocatalytic decomposition reaction of propione aldehyde gas is accelerated by virtue of the effect of a substrate as an adsorbent (see Symposium, "Recent development in Photocatalytic Reaction", previous manuscripts, by Society for the Study of Photofunctional Materials, No. 2-11 page 39, 1994).

[0011] However, no report has been made up till now describing that a substrate having excellent adhesive property and durability while keeping the high photocatalytic activity of a photocatalyst which is uniformly distributed in a metal oxide sol as described above is obtained.

[0012] Whereas, a method to fix a photocatalyst by using a fluororesin has been also proposed (see Japanese Patent Laid-opened No. Hei 6-315614). However, the price of fluororesin is high, and it is required to cover the most of the surface of photocatalyst particles with fluororesin in order to stick photocatalyst particles strongly. Accordingly, the catalytic activity of a photocatalyst becomes lower than the activity given by the same photocatalyst in powder form. Although an example that intends to carry a photocatalyst onto a substrate by means of mixing the photocatalyst with a binder resistant to decomposition, such as fluororesins and poly(organosiloxane), has been known (see EP-0633064) it is not sufficient to solve practically such problems as to adhesive property and durability.

[0013] As described above, the following three points can be given as problems to be solved when carrying a photocatalyst onto a substrate, which are (1) an adhesive property between a photocatalyst and a substrate should be good, (2) the photocatalytic activity of a photocatalyst does not degrade when it is carried onto a substrate and (3) both of a substrate and an adhesive should not be deteriorated due to presence of a photocatalyst carried thereon and the substrate can keep its binding strength, durability and catalytic activity. Furthermore, when using a photocatalyst-carrying structure under a condition of a high temperature and high humidity, a property to maintain excellent adhesive property after dipping it into boiling water is required for the structure, for example.

[0014] Whereas, it is required for a photocatalyst coating material used for carrying a photocatalyst onto a substrate a property that the photocatalyst coating material causes neither its viscosity increase nor its particle sedimentation even after the preservation for at least one month and preferably more than three months. Also, a property that enables to carry a photocatalyst onto a substrate without deteriorating its photocatalytic activity when coating the photocatalyst onto a product for practical use, is required as well.

[0015] The inventors of the present invention have found a method to strongly glue a photocatalyst onto a substrate by providing a specific adhesive layer in between a photocatalyst layer and a substrate to thereby protect the substrate provided under the adhesive layer from its deterioration due to photocatalytic action derived from the photocatalyst and strongly glue the photocatalyst layer to the substrate and by making the adhesive layer resistant to deterioration due to photocatalytic action, providing a solution for the problems as described above.

#### Disclosure of Invention

[0016] The inventors of the present invention found that silicon-modified resin, such as acryl-silicon resin or epoxy-silicon resin, containing 2-60 % by weight of silicon, a resin containing 5-40 % by weight of colloidal silica, and a resin containing 3-60 % by weight of polysiloxane, which is a polycondensation reaction product of a compound represented by a general formula (1);



wherein  $\text{R}^1$  is an alkyl having 1-8 carbon atoms which is unsubstituted or substituted with any of amino, carboxyl or chlorine atom,  $\text{R}^2$  is an alkyl having 1-8 carbon atoms or an alkoxy-substituted alkyl having 1-8 carbon atoms,  $n^1$  is 0, 1 or 2,  $n^2$  and  $n^3$  are each independently 0 or any of integers of from 1 to 3,  $n^4$  is any of integers of from 2 to 4, provided the sum of  $n^1$ ,  $n^2$ ,  $n^3$  and  $n^4$  is 4, can strongly glue a photocatalyst and protect the substrate from photocatalytic action derived from a photocatalyst.

[0017] Moreover, for solving the problem on the photocatalyst coating material, the inventors of the present invention have found out that a photocatalyst coating material comprising 0.001-5 % by weight of one or more of alkoxysilanes represented by a general formula (2);



wherein  $\text{R}^3$  is an alkyl having 1-8 carbon atoms which is unsubstituted or substituted with any of amino, chlorine atom or carboxyl,  $\text{R}^4$  is an alkyl having 1-8 carbon atoms or an alkoxy-substituted alkyl having 1-8 carbon atoms,  $n_5$  is 0, 1 or 2, or the hydrolysis products thereof, 1-30 % by weight of a metal oxide sol and/or a metal hydroxide sol on the solid component basis, and 0.1-30 % by weight of a photocatalyst in powder and/or sol, can be stable for a long time and does not result viscosity increase and particle sedimentation, and they have accordingly accomplished the present invention.

[0018] Furthermore, the inventors of the present invention have also found out that the photocatalyst-carrying structure and the photocatalyst coating material described above can be carried onto various substrates, such as glass, plastics, metals, cloth and woody materials, and can be coated onto lens, adhesive films, window shades, nonwoven fabrics, wooden doors, etc. by using the photocatalyst coating material according to the present invention.

[0019] The present invention is further described in detail in the following.

[0020] In the present invention, a resin to be used for forming the adhesive layer in the photocatalyst-carrying structure is selected from a group consisting of silicon-modified resin, such as acryl-silicon resin or epoxy-silicon resin, com-

prising 2-60 % by weight of silicon, a resin comprising 5-40 % by weight of colloidal silica and a resin comprising 3-60 % by weight of polysiloxane.

[0021] When any of silicon-modified resin containing silicon at content of less than 2 % by weight, such as acryl-silicon resin, a resin containing polysiloxane at a content of less than 3 % by weight and a resin containing colloidal silica at content of less than 5 % by weight is used, the binding force between the adhesive layer and the photocatalyst layer degrades, and the adhesive layer is deteriorated due to the action of a photocatalyst, thereby the photocatalyst layer tends to be exfoliated easily. Whereas, when silicon-modified resin, such as acryl-silicon resin containing silicon at a content more than 60 % by weight is used, the binding between the adhesive layer and the substrate gets worth and the abrasion-resistant property of the structure degrades because of the lowering of the hardness of the adhesive layer.

[0022] Whereas, when a resin containing polysiloxane more than 60 % by weight or a resin containing colloidal silica more than 40 % by weight is used, the adhesive layer becomes porous, the substrate provided under the adhesive layer deteriorates due to the effect of a photocatalyst, and binding condition between the substrate and the adhesive layer degrades, and the photocatalyst layer thereby tends to be easily exfoliated from the substrate.

[0023] When using silicon-modified resin, such as acryl-silicon resin and epoxy-silicon resin, as an adhesive layer material, any silicon-modified resin prepared according to any method for introducing silicon into resin, such as an ester exchange method, graft reaction method using silicon macromers and reactive silicon monomers, hydrosilylation reaction method and block copolymerization method, can be used in the present invention.

[0024] As a resin whereinto silicon is introduced, acryl resin and epoxy resin are the most suitable in terms of film-forming property, toughness and adhesion property to the substrate, however, other resins, such as alkyd resin, urethane resin and polyester resin, can be used as well. In addition, these resins can be used in the either type of solution or emulsion. Also, it is not problematic even though such resin contains an additive, such as a cross-linking agent.

[0025] A photocatalyst-carrying structure with improved adhesive property and durability can be obtained if a resin used for forming an adhesive layer is polysiloxane, and the polysiloxane is a hydrolysis product of a silicon alkoxide having 1-5 carbon atoms or a product derived from such a hydrolysis product. If alkoxy group of the silicon alkoxide contains 6 or more carbon atoms, such resin becomes costly, and the adhesive property and durability of the resin deteriorate because it is difficult to harden the alkoxide in the resin due to its slow hydrolysis rate.

[0026] It is also possible to use polysiloxane which is obtained by subjecting silicon alkoxide partially containing chlorine to hydrolysis, however, a substrate may result corrosion due to the presence of chlorine ions as an impurity when using polysiloxane containing a high degree of chlorine atoms, which also degrades the adhesive property of the adhesive layer.

[0027] As a method to introduce polysiloxane into a resin, a method to mix it in a form of a silicon alkoxide monomer with a resin solution and subsequently allowing it to hydrolysis with moisture in the air at the time of forming an adhesive layer, a method to mix a product obtained by partially allowing silicon alkoxide to hydrolysis with a resin and subsequently allowing the mixture to hydrolysis with moisture in the air at the time of forming a protective film, etc. are known, any method which allows an uniform mixing with a resin can be employed. A small amount of an acid or base catalyst may be added to change the speed of hydrolysis of silicon alkoxide.

[0028] As examples for a resin suitable to be introduced with polysiloxane, acryl resin, acryl-silicon resin, epoxy-silicon resin, silicon-modified resin, urethane resin, epoxy resin, polyester resin, alkyd resin, etc. can be given, however, silicon-modified resin including acryl-silicon resin and epoxy-silicon resin are the most preferable one in view of their durability property.

[0029] If the adhesive layer is composed of a resin that contains colloidal silica, it is preferable if the diameter of colloidal silica particles is 10 nm or less. When the diameter exceeds 10 nm, the resin in the adhesive layer further deteriorates due to the influence of a photocatalyst, and binding condition between the photocatalyst layer and the adhesive layer become worse as well. As a method to introduce such colloidal silica into the resin, it is known that a method to mix a resin solution with a colloidal silica solution, then apply it and subsequently dry it to form an adhesive layer is the easiest, however, a method to form an adhesive layer by allowing a resin to polymerization while dispersing colloidal silica in the resin and then to apply the synthesized resin and dry it, is also acceptable. It is also possible to use colloidal silica after treating it with a silane coupler for improving adhesive property and dispersibility of colloidal silica and a resin.

[0030] As examples for a resin whereinto colloidal silica is introduced, acryl resin, acryl-silicon resin, epoxy-silicon resin, silicon-modified resin, urethane resin, epoxy resin, polyester resin, alkyd resin, etc. are given, however, silicon-modified resins including acryl-silicon resin and epoxy-silicon resin, are the most suitable one in term of durability.

[0031] As the colloidal silica, any silica sol, which is produced either by subjecting sodium silicate solution to cation exchange or by subjecting silicon alkoxide to hydrolysis, can be used.

[0032] Whereas, for a purpose to prevent deterioration of a resin used for an adhesive layer by influence of a photocatalyst and to improve its durability, a mixing of the resin with a photostabilizing agent and/or an ultraviolet absorbent or the like may provide a good effect. As usable photostabilizing agents, it is preferable to use hindered amine compounds, however, any other compounds can be used as well. Whereas, triazole compounds can be used as an ultraviolet absorbent. The amount of the ultraviolet absorbent to be added to the resin is in a range of from 0.005 % by weight

to 10% by weight based on the weight of the resin, and more preferably from 0.01% by weight to 5% by weight. By treating the surface of the adhesive layer with a silane-containing or titan-containing coupler, the binding condition between the adhesive layer and the photocatalyst layer may be improved.

[0033] As a method to carry an adhesive layer on a substrate, a method to coat the substrate with a resin solution according to any of printing method, sheet molding method, spray blowing method, dipping and coating method, spin coating method, etc. and then to dry the coated-substrate can be employed. The temperature for drying the coated-substrate is preferably at 150 °C or less, though it differs depending on type of solvents and resins. When a thickness of an adhesive layer is 0.1  $\mu\text{m}$  or more, it is possible to prepare a photocatalyst-carrying structure which can strongly bind a photocatalyst layer and a substrate and has high durability. Whereas, in case of a coating method, such as gravure method, which requires a process for drying and curing the adhesive layer in a short time, it is also allowable to add a curing agent, such as silicon compounds or the like, into the adhesive layer material from 0.1 to 10% by weight based on the weight of the solid component of the adhesive layer material, depending upon hardening speed required.

[0034] A metal oxide gel or a metal hydroxide gel presenting in a photocatalyst layer provides an effect to fix photocatalyst powder and to strongly adhere it to an adhesive layer, and therefore, a photocatalyst-carrying structure comprising such metal oxide gel and/or metal hydroxide gel show excellent adhesibility, durability and weather resistance as shown in the examples of the embodiment for the present invention. In addition, such metal oxide gel and metal hydroxide gel have porous structure and are adsorbate, and they have further an effect to enhance photocatalytic activity. A preferable range for the content of such metal oxide gel or metal hydroxide gel in the photocatalyst layer is from 25 to 95% by weight. When this content is less than 25% by weight, the binding with an adhesive layer may be insufficient, whereas photocatalytic activity may be insufficient when that content exceeds 95% by weight.

[0035] Furthermore, the binding described above and the photocatalytic activity can be improved, when the specific surface area of the metal oxide gel or the metal hydroxide gel after drying at 150 °C is 50  $\text{m}^2/\text{g}$  or more, and more preferably 100  $\text{m}^2/\text{g}$  or more.

[0036] As examples for a metal in the metal oxide gel and the metal hydroxide gel as described above, silicon, aluminum, titanium, zirconium, niobium, magnesium, niobium, tantalum, tungsten, tin, etc. are given.

[0037] The sticking property of a photocatalyst layer after dipping it into boiling water can be improved by using a metal oxide gel or a metal hydroxide gel comprising 2 or more metals selected from a group consisting of silicon, aluminum, titanium, zirconium and niobium. As examples for a combination of metal components showing boiling water resistance, silicon-aluminum, silicon-titanium, silicon-zirconium, silicon-niobium, aluminum-titanium, aluminum-zirconium, aluminum-niobium, aluminum-tantalum, titanium-zirconium, titanium-niobium, titanium-tantalum, silicon-aluminum-zirconium and silicon-aluminum-titanium are given as preferable, and metal oxide gels and metal hydroxide gels comprising metals, such as silicon-aluminum, silicon-titanium, silicon-zirconium, silicon-titanium-aluminum and silicon-aluminum-zirconium are given as more preferable ones.

[0038] If the specific surface area of these metal oxide gels or metal hydroxide gels is 50  $\text{m}^2/\text{g}$  or more, they provide high sticking property and improved photocatalytic activity to a photocatalyst layer, thereby allowing the photocatalyst-carrying structure to retain excellent binding property even after dipping it into boiling water. In practical uses, both gels prepared by mixing a sol for forming a gel and complex oxide gels prepared by coprecipitation method or the like may be used. For mixing with a photocatalyst, it is desirable either to uniformly mix a metal oxide or hydroxide in a state of sol before forming gel or to mix in a stage of a raw material before preparing a sol.

[0039] As a method to prepare gels, a method to hydrolyze a metal salt, a method to decompose a metal salt by neutralization, a method to exchange ions, a method to hydrolyze a metal alkoxide, and the like can be given, however, any methods by which the gel is obtained in a state that photocatalyst be uniformly dispersed in the gel, are allowable to use. Provided, as the sticking property and the photocatalytic activity of a photocatalyst may be affected if plenty of impurities are contained in the gel, it is preferable to use a gel containing less impurities.

[0040] Further, by adding either of silicon-modified resin or a silane coupler into a photocatalyst layer from 10 to 50% by weight, it is possible to obtain a photocatalyst layer which retains high photocatalytic activity and has an excellent binding property evaluated as more than 6 points according to the adhesive property test, cross-cut Scotch tape test provided in JIS-K5400 even after dipping it into boiling water for 15 minutes.

[0041] The silicon-modified resin or a silane coupler to be added into a photocatalyst layer has an effect to improve the adhesive property of the photocatalyst layer to a substrate in boiling water. As the silicon-modified resin, commonly available resins, such as silicon-acryl resin and silicon-epoxy resin, either in a state of solution in a solvent or suspension in water are usable. Whereas, as the silane coupler, a compound represented by general formulas,  $\text{RSi}(\text{Y})_3$  and  $(\text{R})_2\text{Si}(\text{Y})_2$ , wherein R is an organic functional group and Y is chlorine atom or alkoxy, and the like are usable. In the general formulas described above, methyl, ethyl, vinyl,  $\gamma$ -glycidioxypropyl,  $\gamma$ -methacryloxypropyl,  $\gamma$ -(2-aminoethyl)aminopropyl,  $\gamma$ -chloropropyl,  $\gamma$ -mercaptopropyl,  $\gamma$ -aminopropyl and  $\gamma$ -acryloxypropyl, etc. are given as the examples for a substituent represented by R, and in addition to chlorine atom, any of  $\text{C}_1\text{-C}_6$  alkoxy, such as methoxy, ethoxy,  $\beta$ -methoxyethoxy and  $\beta$ -ethoxyethoxy, are also usable as a substituent represented by Y.

[0042] The amount of silicon-modified resin and a silane coupler to be added to a photocatalyst layer is preferably

from 10 to 50% by weight on the solid component basis. If the such amount is less than 10% by weight, binding property after allowing the layer to boiling water test will be reduced, whereas the added amount exceeds 50% by weight, remarkable decrease in photocatalytic activity may be caused. As the method to add either the silicon-modified resin or the silane coupler into a photocatalyst layer, a method to add such resin into a photocatalyst in a state of either powder or sol and a method to add them into either a metal oxide sol or a metal hydroxide sol which are used for forming a metal oxide gel and added with a photocatalyst. The addition of silicon-modified resin in emulsion to the sol described above is particularly preferable, since it can improve binding property of a photocatalyst layer in boiling water with nearly no decrease of photocatalytic activity.

[0043] Also, an additive, such as a cross-linking agent, can be combined into the silicon-modified resin or the silane coupler.

[0044] As the photocatalyst of the present invention, any type thereof, such as in powder form, sol and solution, can be usable if it can bind with an adhesive layer and show the photocatalytic activity, when it has been dried at a drying temperature for the photocatalyst layer. When a photocatalyst in a sol state is used, it is preferable to use the one of which particle diameter is 20 nm or less, and more preferably 10 nm or less, because the transparency of a photocatalytic layer may be improved and linear permeability thereof increases, and therefore, it is especially preferable to use such photocatalyst for coating of glass substrates and plastic moldings, which are required to be transparent. Furthermore, if color and/or patterns are applied on an underlying substrate, a transparent photocatalyst layer coated with such photocatalyst is advantageous because it does not give adverse influence to colors and/or patterns on the underlying substrates.

[0045] As the photocatalyst to be used for the photocatalyst layer according to the present invention,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SrTiO}_3$ ,  $\text{CdS}$ ,  $\text{GaP}$ ,  $\text{InP}$ ,  $\text{GaAs}$ ,  $\text{BaTiO}_3$ ,  $\text{KNbO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{SiC}$ ,  $\text{SiO}_2$ ,  $\text{MoS}_2$ ,  $\text{InPb}$ ,  $\text{RuO}_2$ ,  $\text{CeO}_2$  and the like, and mixtures of these photocatalysts with a metal or a metal oxide, such as Pt, Rh, Ru,  $\text{O}_2$ , Nb, Cu, Sn, Ni and Fe, can be used. In addition thereto, all mixtures prepared by adding a metal, such as Pt, Rh, Ru,  $\text{O}_2$ , Nb, Cu, Sn, Ni and Fe, into the photocatalyst by using photocatalyst reduction reaction, are also applicable in the present invention. The photocatalytic activity increases along with the increase of content of a photocatalyst in the photocatalyst layer, however, it is preferable to maintain the content to 75% by weight or less in view of maintaining sufficient binding property.

[0046] The photocatalyst coating material according to the present invention is characterized in that the solution comprises silicon compound 0.001-5% by weight, a metal oxide sol and/or a metal hydroxide sol 0.1-30% by weight on the solid component basis and a photocatalyst powder and/or sol 0.1-30% by weight on the solid component basis.

[0047] As the examples for the silicon compounds added to the photocatalyst coating material of the present invention, alkoxy silane represented by a general formula (2),



wherein  $\text{R}^3$  is unsubstituted or substituted alkyl having 1-8 carbon atoms with amino, chlorine atom or carboxyl,  $\text{R}^4$  is an alkyl having 1-8 carbon atoms substituted with alkyl having 1-8 carbon atoms or alkoxy, and  $\text{n}_5$  is any of 0, 1, 2 and 3, and the mixtures with one or more of those hydrolyzed products can be used. In the general formula (2), methyl, ethyl, vinyl,  $\gamma$ -glycidioxypropyl,  $\gamma$ -methacryloxypropyl,  $\gamma$ -(2-aminoethyl)aminopropyl,  $\gamma$ -chloropropyl,  $\gamma$ -mercaptopropyl,  $\gamma$ -amino-propyl,  $\gamma$ -acryloxypropyl and the like are given as the example for the substituent represented by  $\text{R}^3$ , and  $\text{C}_1$ - $\text{C}_8$  alkoxy, such as methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy,  $\beta$ -ethoxyethoxy and 2-ethylhexyloxy, are preferable as examples for the substituent represented by  $\text{OR}^4$ . As the example for the silicon compounds represented by the general formula (2), tetramethoxy silane, tetraethoxy silane, methyltrimethoxy silane, methyltriethoxy silane, and mixtures consisting of one or more hydrolysis products of those compounds mentioned hereinabove can be preferably given.

[0048] By adding a small amount of the silicon compound described above into a coating solution for forming a photocatalyst layer, stable coating material for forming a photocatalyst layer which results in a less increase of viscosity and particles sedimentation even preserving it for a long time can be obtained. As to the amount of the silicon compound to be added to the coating material for forming a photocatalyst layer, it is preferable to add it from 0.001 to 5% by weight on the solid component basis. When the such amount is less than 0.001% by weight, the stability of the coating material for forming a photocatalyst layer becomes lowered when it is preserved for a long time, whereas a prominent decrease in photocatalytic activity will be caused when such amount to add is more than 5% by weight. As a method to add a silicon compound into a coating material for forming a photocatalyst layer, a method to add it into a solution of a photocatalyst in the either form of powder or sol, a method to add it into sol of either a metal oxide or a metal hydroxide, which are added together with a photocatalyst, and the like can be employed. Alternatively, partly-hydrolyzed silicon compounds may be added into the coating material. As the silicon compound to be added into the coating material for forming a photocatalyst layer has an effect to increase the binding property of a photocatalyst in boiling water, it is possible to reduce an amount of the silicon compound to add when the silane coupler as described above or the like has been added into the coating material.



[0049] It is preferable to add a metal oxide sol and/or a metal hydroxide sol 0.1-30% by weight and photocatalyst powder and/or sol 0.1-30% by weight on the solid component basis relative to the weight of the coating material for forming a photocatalyst layer, respectively, into the said coating solution.

[0050] If a ratio of amount of the metal oxide sol and/or the metal hydroxide sol to add is less than 0.1% by weight, property to bind a photocatalyst to a substrate will be insufficient, whereas if the such rate is more than 30% by weight, the amount of photocatalyst powder and/or sol added concurrently is obliged to be reduced, thereby photocatalytic activity will be lowered. Whereas, photocatalytic activity will be too low if a ratio of amount of the photocatalyst powder and/or sol to add is less than 0.1% by weight, and a photocatalyst layer will be easily exfoliated since the amount of a metal oxide sol and/or a metal hydroxide sol for binding the layer to a substrate is obliged to be reduced if a ratio of amount of the photocatalyst powder and/or sol to add is 30% by weight or more.

[0051] The coating material for forming a photocatalyst layer according to the present invention is concurrently used with a coating material for forming an adhesive layer, with which an adhesive layer can be formed in between a photocatalyst layer and a substrate. As the coating material for forming an adhesive layer, a composition which contains from 1 to 50% by weight on the solid components basis a silicon-modified resin containing 2-60% by weight of silicon, a resin containing 3-60% by weight of polysiloxane and a resin containing 5-40% by weight of colloidal silica can be used.

[0052] As a resin suitable to be used for a coating composition for forming an adhesive layer, it is preferable to use the resins usable for an adhesive layer as described above, by alone or in a mixture with any other one of such resins. Such a coating composition is then preferable to be prepared either in solution of an organic solvent or in aqueous emulsion and the content of the resin as a solid element is preferably selected from 1 to 50% by weight. When a coating composition wherein the concentration of solid content of such resin is 1% or less, the adhesive layer is formed too thin and the binding of the photocatalyst layer will be difficult to make. Whereas, when a coating composition wherein the concentration of the solid content of such resin is 50% or more, the adhesive layer will be formed too thick and it will be difficult to properly make a coating film and handle such a coating composition because it will get too much viscous.

[0053] When forming a photocatalyst layer on an adhesive layer, a suspension wherein a photocatalyst is dispersed in a sol of either a metal oxide or a metal hydroxide can be applied by coating according to a method which is the same as the one for forming an adhesive layer. Alternatively, a photocatalyst can be dispersed in a solution of a precursor of either a metal oxide sol or a metal hydroxide sol and is then prepared to a form of either sol or gel through a process of hydrolysis or neutralizing decomposition at the coating process. When the sol prepared as described above is used, a defloculant, such as an acid and an alkali, may be added for improving stability of the sol. Also, it is possible to further improve the adhesive property and easiness in handling by adding a surfactant, silane coupler or the like into the sol 5% by weight or less based on the weight of a photocatalyst. Drying temperature at the time that a photocatalyst layer is formed is preferably from 50 to 200°C though it differs depending upon the difference in substrates and resin materials used for the adhesive layer.

[0054] Though a thicker photocatalyst layer provides higher photocatalytic activity, there is no big difference in the activity if the thickness exceeds 5  $\mu\text{m}$ . The photocatalyst layer of which thickness is 5  $\mu\text{m}$  or less is preferable because it provides high photocatalytic activity and light transmitting property that makes the adhesive layer less conspicuous. However, though light transmitting property is improved in case that a thickness of the photocatalyst layer is less than 0.1  $\mu\text{m}$ , it is not expectable to obtain high photocatalytic activity since ultraviolet ray that can be utilized by a photocatalyst is also penetrated through the photocatalyst layer. Whole light transmittance in total of a photocatalyst layer and an adhesive layer at a wave length of 550 nm will be 70% or more, if a thickness of the photocatalyst layer is set to a range of from 0.1  $\mu\text{m}$  to 5  $\mu\text{m}$  and a photocatalyst of which particles having a diameter of 40 nm or less and either a metal oxide gel or a metal hydroxide gel of which specific surface area is 100  $\text{m}^2/\text{g}$  or more are used. In case of a photocatalyst-carrying structure of which whole light transmittance at a wavelength of 550 nm is 70% or more, visible light penetrating through the structure can be used for illumination, whereas such structure will be useful from the ornamental view point as it does not spoil a design on a substrate if the substrate of such structure is opaque.

[0055] The substrate can be formed in any complex shapes, such as film-like, plate-shaped, tubular, fiber-like and reticular, and the adhesive layer and the photocatalyst layer can be provided to any of the such substrate to thereby form a desired photocatalyst-carrying structure. As to the size of the substrate, it can carry both the adhesive layer and the photocatalyst layer if it has a size of 10  $\mu\text{m}$  or more. Even an organic polymer which is not allowable to be heated at the time of coating and a metal which is easily oxidized and corrosive by heating or with water are used for the materials for the substrate, it is possible to prepare a structure whereto an adhesive layer and a photocatalyst layer are provided, which may show both high photocatalytic activity and high durability. In order to improve the close adherence between a substrate and an adhesive layer, a substrate of which surface is subjected to discharging process, primer process and the like can be used as well.

[0056] As indicated in the examples described below in this specification, the photocatalyst-carrying structure according to the present invention is useful for paints for architectural use, wall papers, window glass, blinds, curtains, carpets, illumination appliances, lightings, black lights, paints for a ship bottom and fishing nets, fillers for water treatment, vinylchloride films for agricultural use, sheets for preventing growth of weeds, packaging materials, etc. In addition, the

photocatalyst-carrying structure can be made to a structure which is usable under a high temperature and highly humid condition.

[0057] According to the present invention, it is possible to provide a structure carrying an adhesive layer and a photocatalyst layer having high durable property being expressed as an evaluating point of 6 or more in an adhesive property test according to a method called cross-cut Scotch tape test provided in JIS K5400 even after exposing it to black light having an ultraviolet radiation intensity of  $3 \text{ mW/cm}^2$  for 500 hours at  $40^\circ\text{C}$  and 90% R. H. Additionally, in an accelerated weathering test by using Sunshine weather meter, a photocatalyst-carrying structure able to show such an excellent weathering resistance being expressed as an evaluating point of 6 or more in an adhesive property test for 500 hours according to said cross-cut Scotch tape test provided in JIS K5400 has been obtained. Furthermore, a structure which shows high resistance to boiling water such that the adhesive property of the structure evaluated by cross-cut Scotch tape test provided in JIS K5400 after dipping in boiling water having an electric conductivity of  $200 \mu\text{S/cm}$  at  $20^\circ\text{C}$  for 15 min. is expressed as an evaluating point of 6 or more. Since high photocatalytic activity is observed in any samples of the structures, it is understood that the structure according to the present invention has satisfactory properties with regard to various uses as described above.

[0058] When a substrate is made of glass, the glass can be formed in any complex shapes, such as plate-shaped, tubular, ball-shaped and fiber-like, and is provided with said adhesive layer and said photocatalyst layer. As to the size, such glass can carry firmly if it is  $10 \mu\text{m}$  or more in size. Moreover, depending upon its usages for, such as window glass, show cases and glasses, it is also possible to apply such layers to the processed glass to thereby make a photocatalyst-carrying glass according to the present invention.

[0059] The photocatalyst-carrying glass according to the present invention can be used for various items which require antimicrobial, deodorant and antisoiling effect, such as cameras and lens for glasses, as well as window glass, cover glass for instruments, illumination appliances, lightings, black light blue fluorescent lamps and fillers for water treatment.

[0060] A plastic molding carrying a photocatalyst according to the present invention can be used for various uses which require antimicrobial, deodorant and antisoiling effect, such as cameras and lens for glasses, as well as wall papers, board for interior decoration, furnishings, electric appliances, and parts for carriages.

[0061] Regarding the shape of the plastic molding described above, any complex shapes, such as film-like, plate-shaped, tubular, ball-shaped and fiber-like, can be used for manufacturing a structure made of plastic molding provided with said adhesive layer and said photocatalyst layer. As to the size, such plastic moldings can carry such layers firmly if its size is  $10 \mu\text{m}$  or more. Furthermore, depending upon the usages, such as for construction materials, electric appliances for home use and glasses, it is also possible to apply such layers to the plastic molding to thereby manufacture a photocatalyst-carrying plastic molding according to the present invention, and therefore, it is understood that the structure of the present invention has substantially a wide application range for use.

[0062] Many kinds of cloth can be used for the substrate of the present invention; textiles, knit cloth, and nonwoven fabrics comprising single or mixed fibers consisting of natural fibers, such as wool, silk, cotton and hemp yarn, regenerated fibers, such as rayon and acetate, synthetic fibers, such as nylon, acrylic, polyamide, polyester, polyacrylonitrile and polyvinyl chloride, and heat-resistant fibers, such as aramid fibers, are given as the examples. Also, as the structure of the present invention, a cloth applied with a water repellent, such as silicon-containing water repellent, fluorine-containing water repellent including perfluoroalkylacrylate, zirconium salt-containing water repellent and ethylene urea-containing water repellent, a cloth treated with both water repellent and a cross-linking agent, such as ethylene imine, epoxy and melamine compounds, for improving durability, if appropriate, an imitation leather consisting of fibril-formed complex fiber of polyamide and polyester, and a synthetic leather wherein a polyurethane resin layer is formed on a substrate, such as textile, nonwoven fabric and knit cloth, via a binder made of polyurethane. Also, by applying such a water repellent and the like to clothes being processed to umbrellas, tents, bags, etc., the photocatalyst-carrying clothes according to the present invention can be obtained.

[0063] The photocatalyst-carrying cloth specified in the present invention is applicable for various uses which require antimicrobial, deodorant and soiling resistant effect, for example, interior decoration, such as curtains and wall papers, tents, umbrellas, daily necessities like table cloth, food package materials and the like, and agricultural use, such as sheets for seedling beds.

[0064] For the photocatalyst-carrying metal according to the present invention, an alloy, such as stainless steel, brass, aluminium alloy and titan alloy, can be used as a substrate as well as single-element metals, such as aluminium, iron and copper. Additionally, in case that it is allowable from the configuration and quality point of view of a metal to use, it is also possible to carry both an adhesive layer and a photocatalyst layer according to the present invention onto the substrate, such as a metal sheet and plate painted with normal colorings, and a colored steel plate or aluminium plate. In this case, it is further preferable that, if the light transmittance of both adhesive layer and photocatalyst layer is sufficiently high and transparent, such layers do not give bad influence to the color on the underlying substrate.

[0065] As to the configuration of the metal, there is no difficulty to make the configuration of the metal into any complex shape, such as plate-shaped, tubular, ball-shaped, fiber-like and sheet-shaped, to carry such adhesive layer and pho-

photocatalyst layer thereon. And, the metal can carry such layers firmly if the size thereof is 10  $\mu\text{m}$  or larger. Furthermore, depending upon the usages, for example, for window flames, show cases and flames for glasses, all of which have been processed, the photocatalyst-carrying metal according to the present invention can be manufactured by applying such layers to the metals having been processed.

5 [0066] The photocatalyst-carrying metal according to the present invention can be used for various uses which require antimicrobial, deodorant and soiling resistant effect, for example, strainers, filters and the like as well as window flames, furnishings, accessories and decoration, panels for interior and exterior decoration, fillers for water treatment, etc.

10 [0067] As to the configuration of timbers and woody materials whereto the adhesive layer and the photocatalyst layer according to the present invention are provided, any complex configuration, such as plate-like, tubular, ball-shaped and sheet-like, can be employed. Such timbers or woody materials can sufficiently carry such layers thereon if their size are 10  $\mu\text{m}$  or larger, and it is allowable to manufacture a photocatalyst-carrying timber or woody material according to the present invention by applying such layers onto the such timber and woody material, such as walls, ceiling boards, columns, furnishings and woodworks, which have been processed beforehand.

15 [0068] The timber and woody material carrying a photocatalyst according to the present invention can be applied for various uses which require antimicrobial, deodorant and soiling resistant effect, for example, for construction materials, furnishings, woodworks, and materials for interior decoration.

20 [0069] By taking advantageous properties, such as soiling resistant, antimicrobial and deodorant function, a plastic film provided with the photocatalyst-carrying structure according to the present invention can be made as films of which face, whereto a photocatalyst is not carried, is applied with an adhesive, and such films can be applied to the inner face of window glass of a structure, such as cars and various transportation means, buildings, freezing and cooling show cases and greenhouses, thereby with such glass allowing to provide highly-transmissible glass which expedites decomposition of trace harmful substance existing in the inner space and has soiling resistant effect on a glass surface and preventive effect to glass spattering at its destruction. When the photocatalyst-carrying structure according to the present invention is prepared by using a thin plastic film as a substrate, it can be used as a wrap film for food package use. As a resin applicable for such plastic films, a resin, such as polyethylene-terephthalate resin, polycarbonate resin, polyacrylate ester resin, polymethylmethacrylate resin, polyethylene resin, polypropylene resin, polyamide resin, polyimide resin, polystyrene resin, poly(vinyl chloride) resin, poly(vinylidene fluoride) resin, ethylene fluoride-propylene copolymer resin and ethylene fluoride-ethylene copolymer resin, which can be molded into a highly transmissive synthetic resin film or sheet of which linear light transmittance at a wavelength of 550 nm is 50% or more can be used. Furthermore, since the photocatalyst-carrying structure according to the present invention is transparent, it does not give bad influence on design and patterns printed on the surface of the underlying wall papers and decoration sheets so that the photocatalyst layer can be applied advantageously onto the surface of an opaque material, such as wall papers and decoration sheets, provided with an adhesive layer and a detachable film layer on its background.

30 [0070] In these synthetic resin films or sheets described above, it is possible to improve the adhesive property of the adhesive layer in the photocatalyst-carrying structure by treating the surface of such films and the sheets, of which surface whereto an adhesive layer is applied, are physically subjected to trace amount oxidation by corona discharge treatment and UV-ozone treatment and the ones of which contact with an adhesive layer are improved by slight application of a surface treating agent, such as silicon-containing compounds, can be used advantageously. In addition, as shown in the examples for the embodiment of the present invention, it is also possible to fix a thin film on the surface or the background of such materials for providing reflecting and shading function against thermic rays and ultraviolet ray, thereby thermic rays reflecting films and ultraviolet ray interrupting films concurrently having soiling resistant, antimicrobial and deodorant function become obtainable. It is understood that the photocatalyst-carrying structure according to the present invention has both excellently high durability and photocatalytic activity, and therefore, it could be exceedingly useful and valuable product.

45 [0071] As a method to provide the thermic rays reflecting function described above, various methods, such as a method to form a film onto a film surface with an electroconductive metal, such as Al, Ag, Cu, Cr, Ni, Ti, stainless and aluminium alloy, or an electroconductive metal oxide, such as indium oxide, tin oxide and tin oxide-indium oxide compound, according to a physical means, such as sputtering and vacuum evaporation, a method to form a film onto a film surface by means of applying and then drying an electroconductive metal oxide solution or sol onto the film surface or employing either plating method or CVD method and a method to admix a material having thermic rays reflecting property and/or thermic rays interrupting property into the substrate, can be employed. Yet, as a method to provide ultraviolet ray interrupting function, various methods, such as a method to form a film onto a film surface by applying an ultraviolet ray absorbent, such as hindered amine-containing compounds and titanium oxide, and an ultraviolet ray reflecting agent and a method to admix an ultraviolet ray absorbent into a film substrate beforehand, are allowed to employ and is selectable depending upon its use purpose and chemical structures. When titanium dioxide is used as ultraviolet ray blocker or ultraviolet ray reflecting agent, it is preferable to use the one which has lost its photocatalytic activity due to slight coating of the surface of titanium dioxide with soluble glass or the like, because surrounding organic materials are decomposed due to photocatalytic action if titanium dioxide is existing alone, as explained in detail in the

present invention.

[0072] Materials having thermic rays reflecting function and ultraviolet ray blocking function can be incorporated into a sticker layer which is formed on the background of a film to provide such functions. For example, a material like ultraviolet blocking clear coating agent described in "Convertec", March 1996, page 95, is solvent-dispersible type and is applicable for the above purpose. Stickers, such as acrylic-type and silicon-containing compounds are normally used, however, it is also feasible to add various types of ultraviolet ray blocking agents and thermic rays blocking agents. Considering spoil caused with the remaining sticker at the time of renewal the photocatalyst carrying film, it is advisable to avoid the use of a sticker having strong binding property. As a method to provide a sticker and a detachable film onto a photocatalyst-carrying film, a method to firstly coat a sticker in solution to the reverse side of the film by means of gravure printing and then dry and roll the coated-film together with detachable polypropylene film while laminating it therewith is simple and may be preferably employed.

Brief Description of Drawings

[0073]

Fig. 1 is a chart for the cross section of the photocatalyst-carrying structure according to the present invention.

Best Mode for Carrying Out the Invention

[0074] The present invention is definitely explained with referring the examples described below, however, the present invention should not be limited to the scope described in such examples.

( Evaluation Method )

1) Evaluation of Photocatalytic Activity

[0075] A sample carrying a photocatalyst with a dimension of 70 mm × 70 mm is placed in a 4-liters Pyrex glass container. A mixed gas consisting of air and acetaldehyde was introduced in this container and the concentration of the acetaldehyde was set to 500 ppm. The sample was exposed to black light (Type: FL 15BL-B; Manufactured by Matsushita Electric Industry Co., Ltd.) with an ultraviolet ray intensity of 2 mW/cm<sup>2</sup> for 2 hours. Then, a concentration of acetaldehyde gas in the container was determined by using gas chromatography, and photocatalytic activity was determined based on the decreased amount of the concentration. Criterion for the evaluation was provided as follows.

Acetaldehyde Gas Concentration after 2 Hours	Evaluated Rank
< 50 ppm	A
50 - 200 ppm	B
200 - 300 ppm	C
300 - 450 ppm	D
450 ppm <	E

2) Evaluation of Adhesive Property

[0076] Evaluation of adhesive property was carried out according to cross-cut Scotch tape test which is provided in JIS K 5400. A distance between cross-cut lines set to 2 mm, and the number of squares is fixed to 25.

[0077] Evaluated point was accorded to a criterion described in JIS K 5400.

3) Dipping Test into Boiling Water

[0078] Tap water with an electric conductivity ranging from 170 to 230  $\mu$ S/cm was placed into a 1000 ml Pyrex glass beaker together with small amount of zeolite, the sample cut into a size of 70 mm × 70 mm was hanged into boiling water by using a normal clip to let the whole sample sink into water after heating and boiling water. After 15 min. dipping

in boiling water, the sample was allowed to cooling and drying at a room temperature for 4 hours, then the adhesive property test described in the paragraph 2) was conducted to obtain evaluated-points according to the criterion described in JIS K 5400.

#### 4) Whole Light Transmittance

[0079] Whole light transmittance at a wavelength of 550 nm of the sample carrying an adhesive layer and a photocatalyst layer was measured by using an automatically-recording spectrophotometer (Type: U-4000, Manufactured by Hitachi Seisakusho) with referring a substrate which has not yet carried an adhesive layer and a photocatalyst layer.

#### 5) Evaluation of Durability

[0080] The carrying sample was allowed to radiation of black light with an ultraviolet ray intensity of 3 mW/cm<sup>2</sup> for 500 hours in a chamber maintained at 40°C and 90% R. H., then the adhesive property test described in the paragraph 2) was conducted to obtain evaluated-points according to the criterion described in JIS K 5400.

#### 6) Accelerated Weathering Test by Using Sunshine Carbon Arc Weather Meter

[0081] Accelerated weathering test by using sunshine carbon arc weather meter provided in JIS K 5400 was conducted by using the same meter (Type: WEL-SUN-HCH; Manufactured by Suga Shikeni Co., Ltd.) at a condition, namely, test duration of 500 hours, black panel temperature of 63 °C, 120 min. cycle and 18 min. rainfall. 3 pieces of the samples were allowed to the accelerated weathering test, then the samples were visually evaluated in terms of swelling, cracking, peeling off, whitening and surface change in comparison with the original test pieces which are before subjecting it to the accelerated weathering test according to the following criterion.

Evaluated-rank	Criterion for Evaluation
A	All of 3 samples showed no change.
B	1 or 2 samples showed slight change.
C	All of 3 samples showed slight change, or 1 or 2 samples showed apparently great change.

[0082] After conducting this test, the adhesive property test as described in the paragraph 2) was then conducted to obtain evaluated-points according to a criterion described in JIS K 5400.

#### 7) Test Method for Antimicrobial Property

[0083] The sample cut into a piece with a dimension of 5 x 5 cm is disinfected with 80% ethanol and then dried at 150 °C and 0.2 ml of a bacterial suspension of colon bacillus, which was cultivated and diluted beforehand, to a concentration of 10<sup>5</sup>/ml was fed dropwise to the surface of the sample and placed in an incubator. For each radiation condition, 4 samples were provided for the test, respectively, namely, 4 samples for black light radiation (15W x 2 lamps, distance between a light source and the sample is 10 cm), 4 samples for fluorescent lamp radiation (15W x 2 lamps, distance between a light source and the sample is 10 cm), and an other 4 samples for no light radiation were provided. After predetermined time lapsed (after 1, 2, 3 and 4 hours), the samples were taken out and the bacterial solution attached to the samples was wiped off by using disinfected gauze rinsed in sterilized physiological saline solution. The sterilized gauze used was put into 10 ml sterilized physiological saline and thoroughly stirred. The supernatant of the bacterial solution obtained was inoculated to an agar medium prepared in a petri dish having a diameter of 95 mm which is sterilized by using an autoclave. Then, number of the colonies of colon bacillus cultivated at 36°C for 24 hours was counted. Another sample obtained according to the same procedure from dropping of the bacterial solution through placing into an incubator was treated according to the same method as described above, and the number of colonies of colon bacillus was counted. Based on the counted-number, the survival rate of the bacteria after each predetermined time was calculated for each group exposed to no light, black light and fluorescent lamp, respectively. The evaluation criterion accorded to the following.

Survival Rate (%) of Clon Bacillus after 4 Hours	Evaluated-rank
< 20 %	A
20 - 40%	B
40 - 60%	C
60 - 80%	D
80% <	E

#### 8) Evaluation of Soiling Resistant Property (Decomposition Activity of Fat and Oil)

[0084] As an index to evaluate soiling resistant function of the sample, a decomposed amount of common salad oil mainly composed of linoleic acid on a photocatalyst-carrying structure was qualitatively determined in order to know how fast can fat and oil attached on the surface be decomposed. To the surface of a photocatalyst-carrying structure cut into pieces with a dimension of 5 x 5 cm, salad oil was applied slightly at a dose of 0.1-0.15 mg/cm<sup>2</sup> by using a paper. The quantity applied was calculated from the difference of the weight of the structure before and after an application of oil that were measured by using an accurate balance. As an index of soiling resistant property, decomposed amounts of salad oil after predetermined time were determined by adjusting the distance between the sample and black light to take a point where an ultraviolet ray intensity on a surface of the sample becomes 3 mW/cm<sup>2</sup> and calculating the relationship between lapsing time and weight decrease amount after lighting black light.

Remaining rate (%) of Salad Oil after 24 Hours Light Irradiation	Evaluated-rank
< 10%	A
30 - 10%	B
50 - 30%	C
80 - 50%	D
80% <	E

#### ( Examples )

[0085] As a material for a substrate the following were used.

- (TA) Primer-treated polyester film
- (TB) Vinyl chloride film
- (TC) Soda lime glass plate
- (TD) Metal aluminium plate
- (TE) High-density polyethylene mesh  
(Thickness of fiber: 0.2 mm, Mesh size: 0.6 mm)
- (TF) Polypropylene tube  
(Inner diameter: 30 mm, Outer diameter: 36 mm)

[0086] As polysiloxane contained in an adhesive layer, the followings were used.

- (PS-1) Silicon tetramethoxide monomer (Manufactured by Shinetsu Chemical Industry Co., Ltd.)
- (PS-2) Polymethoxy siloxane (Manufactured by Colcoat Co., Ltd., Trade Name: Methyl silicate 51)
- (PS-3) Polyethoxy siloxane (Manufactured by Colcoat Co., Ltd., Trade Name: Ethyl silicate 40)

[0087] As colloidal silica contained in an adhesive layer, the followings were used.

- (KS-1) Trade Name: Cataloid SI-350 (Manufactured by Shokubai Kagaku Co., Ltd., Particle diameter: 7-9 nm)  
 (KS-2) Trade Name: Snowtex ST-XS (Manufactured by Nissan Chemical Industries Co., Ltd., Particle diameter: 4-6 nm)

[0088] As a resin solution whereto polysiloxane or colloidal silica is introduced, the followings were used.

- (J-1) 3% by weight of silicon containing acryl-silicon resin solution in xylene  
 (J-2) 10% by weight of silicon containing acryl-silicon resin solution in xylene  
 (J-3) 20% by weight of silicon containing acryl-silicon resin emulsion in water  
 (J-4) 50% by weight of silicon containing acryl-silicon resin emulsion in water  
 (J-5) 10% by weight of silicon containing polyester-silicon resin solution in xylene  
 (J-6) Acryl resin solution in xylene  
 (J-7) Polyester resin solution in xylene  
 (J-8) 3% by weight of silicon containing epoxy-silicon resin solution in methyl ethyl ketone

[0089] Either polysiloxane or colloidal silica was mixed with a resin solution, and the mixture obtained was diluted to a certain concentration to thereby prepare a solution to be used for forming an adhesive layer. The adhesive layer was formed by employing dipping method when a thickness of the layer is 2  $\mu\text{m}$  or less and the configuration thereof is other than plate-like, whereas it is formed by using baker applicator when the thickness is 2  $\mu\text{m}$  or more and the configuration thereof is plate-like. In particular, the adhesive layer is formed according to dipping method when the configuration of the substrate is tubular or reticular. Drying process for the adhesive layer was taken place at 80 °C when the material of the substrate is (TE) or (TF), and at 60°C when the material is (TB), and at 120°C in all other cases.

[0090] For the photocatalyst, the following materials were used.

- (C-1) Fine powder of titanium dioxide (Manufactured by Nihon Aerosil Co., Ltd., Trade Name: P-25, diameter of crystallite size: 27 nm)  
 (C-2) Titanium dioxide sol (sol acidified with nitric acid, diameter of crystallite size: 10 nm)  
 (C-3) Titanium dioxide sol (weak alkaline sol of pH 9.0, diameter of crystallite size: 20 nm)

[0091] A metal oxide sol or a metal hydroxide sol carried together with a photocatalyst was obtained by drying any of the following materials in sol.

- (Z-1) Silica sol: Manufactured by Shokubai Kasei Co., Ltd., Trade Name: Cataloid SI-30, specific surface area after drying at 150 °C: 180  $\text{m}^2/\text{g}$   
 (Z-2) Alumina sol: Manufactured by Nissan Chemical Industries Co., Ltd., Trade Name: Alumina Sol-200, specific surface area after drying at 150 °C: 400  $\text{m}^2/\text{g}$   
 (Z-3) Zirconia sol: This is obtainable by allowing zirconium tetrabutoxide (TBZR; Manufactured by Nippon Soda Co., Ltd.) to hydrolyzation in ethanol, drying at 150°C, then heating at 300-500 °C, and further allowing to deflocculation with a diluted aqueous solution of nitric acid. Specific surface area of further dried product at 150 °C of the deflocculated-sol is in a range of from 50 to 80  $\text{m}^2/\text{g}$ .  
 (Z-4) Niobium oxide sol: This is obtainable by allowing aqueous solution of niobium oxalate manufactured by CBMM Co., Ltd. to neutralization with 10% aqueous ammonia, drying at 150°C, and then allowing to deflocculation with a diluted aqueous solution of nitric acid. Specific surface area of further dried product at 150°C of the deflocculated-sol is 60  $\text{m}^2/\text{g}$ .  
 (Z-5) 20% by weight of silicon containing acryl-silicon resin emulsion in water  
 (Z-6) Si lane coupler, tri( $\beta$ -methoxyethoxy)vinyl silane (Trade Name: A-1 72), manufactured by Nippon Uniker Co., Ltd.

[0092] A solution used for forming a photocatalyst layer was prepared by dispersing titanium dioxide into the solution obtained as described above and adding a predetermined amount of a surfactant. The photocatalyst layer was formed by dipping method when the thickness of the layer is 2  $\mu\text{m}$  or less and/or the configuration of a substrate is the one other than plate-like, whereas the photocatalyst layer was formed by using bar coater when the substrate is plate and its thickness is 2  $\mu\text{m}$  or more. Drying process for the photocatalyst layer was taken place at the same temperature as for drying the adhesive layer.

[0093] Hereunder, compositions disclosed in the examples for the embodiment of the present invention and reference examples, wherein type, quantity and/or thickness of materials, and/or method for forming films are different, and per-

formances of the photocatalyst-carrying structure are described in Tables 1 through 4.

[0094] In the examples 1 through 18 and the reference examples 1 through 4, titanium dioxide (P-25) manufactured by Nihon Aerosil Co., Ltd., which is represented at (C-1), was used as a photocatalyst. The result is shown in Table 1.

Table 1

Carrier	Adhesive Layer						Photocatalyst Layer		Thick- ness of Adhesive Layer ( $\mu\text{m}$ )	Thick- ness of Photocat- alyst Layer ( $\mu\text{m}$ )	Photo- catalytic Activity	Adhesive Property		Whole Light Trans- mittance (%)
	Polyisocyanate		Colloidal Silica		Resin Solvent	Metal Oxide Sol								
	Type	Content % <sup>*1</sup>	Type	Content % <sup>*1</sup>		Type	Content % <sup>*2</sup>							
Example-1	TA	-	-	-	J-2	B-1	50	10	3	B	8	6	82	
Example-2	TC	-	-	-	J-5	B-1	75	5	5	B	10	8	75	
Example-3	TA	PS-1	10	-	J-1	B-1	50	5	3	A	10	10	82	
Example-4	TA	PS-1	20	-	J-2	B-1	75	5	5	A	10	10	80	
Example-5	TC	PS-2	5	-	J-1	B-1	50	1	0.5	A	10	10	90	
Example-6	TB	PS-2	20	-	J-2	B-1	30	5	2	A	10	8	85	
Example-7	TA	PS-2	50	-	J-6	B-1	70	1	0.5	B	8	8	90	
Example-8	TC	PS-2	20	-	J-2	B-1	50	(*)3	C	(*)4	(*)4	(*)5	(*)5	
Example-9	TP	PS-2	35	-	J-5	B-1	60	10	5	A	10	10	(*)5	
Example-10	TD	PS-3	20	-	J-1	B-1	50	10	7	A	10	8	(*)5	
Example-11	TD	PS-3	20	-	J-2	B-2	80	5	1	B	10	8	(*)5	
Example-12	TA	PS-3	10	-	J-7	B-1	50	10	5	A	8	8	72	

\*1: Percent by weight as SiO<sub>2</sub> contained in a dried adhesive layer.

\*2: The measurement of thickness could not be done.

\*3: The measurement of thickness could not be done.

\*4: No detachment was observed after ultrasonic irradiation for 10 min.

\*5: The detachment could not be made because of complex configuration and shape property of the carrier.

\*6: In example 35, 60 weight silicon-alumina component is compared at this ratio before and is used.



Table 1 (Continued)

Carrier	Adhesive Layer						Photocatalyst Layer		Thick- ness of Adhesive Layer ( $\mu\text{m}$ )	Thick- ness of Photo- catalyst Layer ( $\mu\text{m}$ )	Photo- catalytic Activity	Adhesive Property		Whole Light Trans- mittance (%)
	Polysiloxane		Colloidal Silica		Resin Solvent	Metal Oxide sol								
	Type	Content % <sup>1</sup>	Type	Content % <sup>1</sup>										
							Type	Content % <sup>2</sup>						
Example-13	TA	-	KS-1	20	J-3	Z-1	50	10	3	A	10	8	82	
Example-14	Tb	-	KS-1	10	J-4	Z-1	40	10	5	A	8	6	75	
Example-15	TA	-	KS-2	20	J-3	Z-1	50	5	3	A	10	8	82	
Example-16	TD	-	KS-2	35	J-4	Z-1	50	2	1	B	10	10	(*)	
Example-17	TA	-	KS-2	10	J-3	Z-1	50	0.5	0.1	C	10	10	90	
Example-18	TC	-	KS-2	20	J-7	Z-1	70	5	2	B	8	6	72	
Reference Example-1	TA	-	-	-	-	Z-1	50	-	2	B	0	0	50	
Reference Example-2	TA	PS-2	70	-	J-1	Z-1	50	5	3	E	(*)	(*)	(*)	
Reference Example-3	TC	-	KS-2	50	J-3	Z-1	50	5	2	B	2	0	10	
Reference Example-4	TC	PS-2	20	-	J-2	Z-1	20	5	5	A	2	2	20	

<sup>1</sup>: Percent by weight as SiO<sub>2</sub> contained in a dried adhesive layer.

<sup>2</sup>: Percent by weight of either a metal oxide gel or a metal hydride gel contained in a dried adhesive layer.

<sup>3</sup>: The measurement of thickness could not be done.

<sup>4</sup>: No detachment was observed after ultrasonication for 10 min.

<sup>5</sup>: The determination could not be made because of complex configuration and opaque property of the carrier.

<sup>6</sup>: The determination could not be made because the photocatalyst layer was etiolated at the time of formation.

In this case, the photocatalyst layer has no sticking property and is easily defoliated. Furthermore, after durability test, the surface of polyester film deteriorated due to a photocatalytic effect, and holes and cracks were observed on the film.

[0096] In examples 1 and 2, a structure wherein either acryl-silicon resin or polyester-silicon resin is used as an adhesive layer is given. In this case, the adhesive property of a photocatalyst layer and durability of the structure was found to be excellent.

[0097] In examples 3 through 12, a structure wherein a resin containing polysiloxane is used as the adhesive layer is given. In this case, adhesive property and durability was improved. As well as the resin containing polysiloxane, acryl-silicon resin (see examples 3, 4 and 5) and polyester-silicon resin (see example 9) had also acquired good durability. Further, the resin containing polysiloxane was found to be replaceable with either acryl resin (see example 7) or polyester resin (example 12), both of which provided excellent property to the structure.

[0098] Contrary, as shown in reference example 2, even though using acryl-silicon resin containing polysiloxane for the adhesive layer, a photocatalyst layer lost its adhesive property and was defoliated from the adhesive layer when the content of polysiloxane in the adhesive layer is increased up to 70% by weight.

[0099] In examples 13 through 18, a structure wherein a resin containing colloidal silica was used as the adhesive layer is given. In these cases, all of photocatalytic activity, adhesive property and durability were found to be excellent. In particular, when acryl-silicon resin and colloidal silica in fine particle size (KS-2) were used (examples 15 and 16), the resulting adhesive layer was found to be very good.

[0100] Contrary, when increasing the content of colloidal silica in the adhesive layer up to 50% by weight, both adhesive property and durability were become worse radically.

[0101] In examples 1 through 18, titanium dioxide (P-25) manufactured by Nihon Aerosil Co., Ltd. represented by (C-1) was used as a photocatalyst, and silica sol was used in most cases as a metal oxide sol or a metal hydroxide sol to be compounded to the photocatalyst layer, and the structures in all examples are provided with excellent properties. In examples 8 and 9, the structures wherein both layers are carried on a substrate made of polyethylene mesh or polypropylene tube were disclosed, and it is demonstrated that these structures show excellent photocatalytic activity, adhesive property and durability. It is also found that such excellent property was still noticeable even decreasing the content of silica sol in the photocatalyst layer down to 30% by weight (see example 6), however, both adhesive property and durability radically deteriorated when reducing the content down to 20% by weight (see example 4).

[0102] In example 11, a structure wherein alumina sol was used instead of silica sol is given, and this structure is also found as excellent in the property as well as using silica sol.

[0103] In example 17, a structure wherein a thickness of an adhesive layer and a photocatalyst layer was set to 0.5  $\mu\text{m}$  and 0.1  $\mu\text{m}$ , respectively. In this case, both adhesive property and durability were excellent, and photocatalytic activity was found to be very high even the thickness of the photocatalyst layer was very thin.

[0104] Data obtained in examples 19 through 23 are shown in Table 2.

Table 2

	Carrier	Adhesive Layer			Photocatalyst Layer	Thick- ness of Adhesive Layer ( $\mu\text{m}$ )	Thick- ness of photo- catalyst Layer ( $\mu\text{m}$ )	Photo- catalytic Activity	Adhesive Property		Whole Light Trans- mittance (%)	
		Polysiloxane Type	Resin Solvent Type	Metal Oxide Sol Type					Content *2	Before Durability Test		After Durability Test
					Content *1							
Example-19	TC	PS-2	35	J-1	2-1	50	5	3	A	10	10	93
Example-20	TC	PS-2	35	J-1	2-3 **	50	5	3	A	10	10	82
Example-21	TA	PS-2	35	J-5	2-1	60	3	3	A	10	10	95
Example-22	TC	PS-2	35	J-5	2-1	60	3	2	A	10	10	90
Example-23	TA	PS-3	10	J-8*	2-1	50	10	5	A	10	10	80

\*1: Percent by weight as  $\text{SiO}_2$  contained in a dried adhesive layer.

\*2: Percent by weight of either a metal oxide gel or a metal hydroxide gel contained in a dried adhesive layer.

\*3: An uniform solution prepared by mixing alumina sol and silica sol at a mixing ratio of 1:1 was used.

\*4: Methyl ethyl ketone solution of epoxy-silicon resin containing 3% by weight of silicon was used.

## Example 19 Use of Titania Sol

[0105] A coating material to be used for forming a photocatalyst layer was prepared by adding and dispersing titania sol containing 12% by weight of titanium dioxide and acidified with nitric acid, which is a substitute of fine granule titanium dioxide (P-25) manufactured by Nihon Aerosil Co., Ltd., into silica gel (Trade name: Cataloid SI-30. Manufactured by Shokubai Kasei Co., Ltd.) being adjusted to pH 1.5 and then further adding a surfactant. Whereas, a solution to be used for an adhesive layer was prepared by adding polymethoxy siloxane (PS-2) into a resin solution used in the example 10 at a rate such that the content of silicon oxide in a dried adhesive layer becomes 35% by weight.

[0106] The solution for forming an adhesive layer was applied by using a baker applicator onto a soda lime glass substrate with a thickness of 1 mm and a dimension of 7 cm x 7 cm, and the coating material for forming a photocatalyst layer was also applied by using bar coater onto the same substrate. Drying temperature was set to the same employed in the examples described above.

[0107] The photocatalyst-carrying structure obtained was found to have very high whole light transmittance.

## Example 20 Use of Silica-alumina Sol

[0108] A photocatalyst-carrying structure was prepared by using the same materials and according to the same method as described in the example 19 except replacing silica sol used in the example 19 with a mixed sol solution consisting of alumina sol manufactured by Nissan Chemical Industries Co., Ltd. and silica sol.

[0109] The photocatalyst-carrying structure obtained was found to have high adhesive property and photocatalytic activity.

## Example 21 Coating according to Gravure Printing Method

[0110] By using gravure printing system, the solution for forming an adhesive layer and the solution for forming a photocatalyst layer were applied onto a polyester film (Trade name: Cosmoline A4100) manufactured by Toyobo Co., Ltd. at a speed of 10 m/min, and at dry zone temperature of 130°C such that the thickness of each layers become 3 µm, respectively. For the printing, a microgravure coater with a width of 70 cm manufactured by Yasui Seiki Co., Ltd. was used.

[0111] The photocatalyst-carrying structure obtained was found to have very high whole light transmittance of 95%.

## Example 22 Coating according to Spraying Method

[0112] The solution for forming an adhesive layer and the solution for forming a photocatalyst layer used in the example 9 were sprayed onto a substrate made of soda lime glass by using a spray gun (Type: WIDER 88, Manufactured by Iwata Tosoki Kogyo K.K.). Both solutions for forming adhesive layer and for photocatalyst layer were dried at 120 °C for 30 minutes.

[0113] The photocatalyst-carrying structure obtained was found to have good adhesive property and photocatalytic activity.

## Example 23 Use of Epoxy-silicon Resin

[0114] A photocatalyst-carrying structure was prepared by using the same materials and employing the same method as described in the example 12 except replacing the polyester resin solution in xylene with methy ethyl ketone solution of epoxy resin containing 3% by weight of silicon.

[0115] The photocatalyst-carrying structure obtained was found to have good adhesive property and photocatalytic activity.

[0116] The compositions and the results of performance tests on the photocatalyst-carrying structures are presented in Table 3.



## Examples 24 - 25

[0117] In examples 24 and 25, a structure, wherein acryl-silicon resin is used for forming an adhesive layer, and a mixture prepared and composed with 50% by weight of fine granule titanium dioxide P-25 (C-1), 25% by weight of silica sol represented at (Z-1) and 25% by weight of alumina sol represented at (Z-2) are used for forming a photocatalyst layer, is disclosed. The structures disclosed in these examples were found to have good adhesive property as well as good durability and resistant property under accelerated weathering condition.

## Examples 26 - 31

[0118] In examples 26 through 31, a structure, wherein a resin containing polysiloxane was used for forming an adhesive layer, and for forming a photocatalyst layer, fine granule titanium dioxide (C-1) was used in examples 26 through 28 while titania sol (C-2) was used in examples 29 through 31, and the type and the quantity of a sol for forming a compoundable gel were changed, is disclosed. The structures prepared in these examples were found to have good photocatalytic activity as well as good adhesive property, durability and resistant property against accelerated weathering tests following to receiving boiling water test. The resins introduced with polysiloxane, such as acryl-silicon resin (examples 26, 27 and 28) and epoxy-silicon resin (examples 29 and 30), were found to have good adhesive property, durability and resistance against accelerated weathering. Also, acryl resin introduced with polysiloxane (example 31) was found to have good properties.

## Examples 32 - 35

[0119] In examples 32 and 33, a structure, wherein either polyethylen mesh or polypropylene tube was used as the substrate was presented, however, the photocatalyst-carrying structure having good photocatalytic activity, adhesive property and durability was not obtained.

[0120] In examples 32 through 35, structures, wherein a resin containing colloidal silica was used for forming an adhesive layer, are disclosed, and photocatalytic activity, adhesive property, durability and resistance against accelerated weathering of such structures were found to be excellent. In particular, when the structure is prepared with colloidal silica in fine particles (KS-2) and the colloidal silica is introduced into acryl-silicon resin emulsion (see examples 34 and 35), this type of structure was found to have very good properties.

[0121] In example 29, a structure, wherein a photocatalyst layer was formed with a coating material prepared by dispersing titania sol containing 12% by weight of titanium dioxide, silica gel (Trade name: Cataloid SI-30, manufactured by Shokubai Hasei Co., Ltd.) and alumina sol-200 manufactured by Nissan Chemical Industries Co., Ltd., adjusting the pH of the resulting mixture to 1.5 and adding a predetermined amount of a surfactant to the mixture, and the thickness of an adhesive layer and a photocatalyst layer was made to 0.5  $\mu\text{m}$  and 0.3  $\mu\text{m}$  by dipping method, respectively, is disclosed. The structure provided with the layers as described above was found to have good adhesive property and durability as well as high photocatalytic activity, nonetheless of the thin thickness of the photocatalyst layer.

[0122] A structure with excellent physical property was also obtained even if contents in total of silica gel and alumina sol in a photocatalyst were reduced down to 30% by weight (see example 30).

[0123] Photocatalytic activity was determined again on the samples, which were prepared in the examples 24 through 35 and were allowed to a durability test under black light at a high temperature and high humidity, dipping test in boiling water and accelerated weathering test by using Sunshine carbon arc weather meter, according to the same method as described above, namely based on the decomposed amount of acetaldehyde by light. As a result, it is found that all samples showed equivalent decomposing activity to the initial decomposed-amount of acetaldehyde, and it is found that the samples have fully kept their initial photocatalytic activity.

[0124] The compositions and performance test results on the photocatalyst-carrying structures disclosed in the examples 36 through 53 are presented in Tables 4 and 5.

Table 4

	Carrier	Adhesive Layer			Photocatalyst Layer						Adhesive Layer Thickness ( $\mu$ )	Photocatalyst Layer Thickness ( $\mu$ )	
		Type	Content #1	Resin Sol.	Titanium Dioxide Type	Content #2	Z-1 Content #2	Z-2 Content #2	Z-3 Content #2	Z-5 Content #2			Z-6 Content #2
Example-36	TA	—	—	J-1	C-1	50	40	—	—	10	—	10	6
Example-37	TB	—	—	J-1	C-1	40	40	—	—	20	—	10	6
Example-38	TA	PS-1	15	J-1	C-1	40	10	—	—	10	—	7	7
Example-39	TB	PS-1	30	J-1	C-1	25	—	—	—	50	—	7	3
Example-40	TC	PS-1	45	J-2	C-1	20	30	10	10	30	—	3	3
Example-41	TB	PS-1	10	J-2	C-1	25	50	—	10	15	—	5	3
Example-42	TA	PS-2	20	J-2	C-1	40	30	10	—	10	10	3	1
Example-43	TB	PS-2	30	J-8	C-1	40	20	10	—	20	10	0.6	0.2
Example-44	TD	PS-2	45	J-7	C-2	50	20	—	10	20	—	5	3
Example-45	TE	PS-2	10	J-1	C-2	50	20	10	—	—	20	6	6
Example-46	TB	PS-2	20	J-8	C-2	25	30	25	—	—	20	5	3
Example-47	TB	PS-3	30	J-6	C-2	60	10	10	—	15	5	3	3
Example-48	TA	KS-1	10	J-3	C-1	30	20	10	—	35	5	10	6
Example-49	TB	KS-1	20	J-4	C-1	50	30	10	—	5	5	5	3
Example-50	TC	KS-2	30	J-3	C-1	20	30	10	—	30	10	5	3
Example-51	TB	KS-2	40	J-4	C-2	30	40	20	—	10	—	3	3
Example-52	TD	KS-2	20	J-3	C-2	60	20	—	—	20	—	5	3
Example-53	TE	KS-2	30	J-3	C-2	20	40	—	10	30	—	5	2
Reference Example-5	TA	—	—	—	C-1	40	30	10	—	20	—	10	10
Reference Example-6	TB	PS-1	70	J-1	C-1	40	30	10	—	20	—	10	6
Reference Example-7	TA	KS-1	50	J-3	C-1	40	30	10	—	20	—	10	6
Reference Example-8	TB	PS-1	30	J-1	C-1	45	30	20	—	5	—	7	3

\* 1 : % by weight as SiO<sub>2</sub> in a dried adhesive layer.

\* 2 : % by weight of titanium dioxide and either a metal oxide gel or a metal hydroxide gel in total in a dried photocatalyst layer.

Table 5

	Photocatalytic Activity	Adhesive Property		Adhesive Property After Boiling Water Test	Sunshine Weather Meter		Whole Light Transmittance (%)
		Before Durability Test	After Durability Test		State of Surface After Test	Adhesive Property After Test	
Example-36	A	10 pt.	8 pt.	10 pt.	A	8 pt.	68
Example-37	A	10	8	10	A	8	65
Example-38	A	10	10	8	A	8	63
Example-39	B	10	10	8	A	8	75
Example-40	B	10	10	10	A	8	-5
Example-41	B	10	8	8	A	6	71
Example-42	C	10	10	10	A	8	82
Example-43	C	10	8	8	A	6	87
Example-44	B	-3	-3	-3	A	-3	-4
Example-45	A	10	10	8	A	8	-4
Example-46	B	10	8	10	A	6	75
Example-47	B	10	8	8	A	6	70
Example-48	A	10	8	8	A	8	66
Example-49	B	10	8	8	A	8	77
Example-50	B	10	8	10	A	8	-5
Example-51	B	10	8	10	A	8	83
Example-52	B	-3	-3	-3	A	-3	-4
Example-53	C	10	8	10	A	6	-4
Reference Example-5	A	2	2	0	C	0	54
Reference Example-6	A	4	2	2	C	2	52
Reference Example-7	A	4	2	2	C	2	48
Reference Example-8	B	4	4	2	C	4	51

\* 3 : Since cross-cut Scotch tape test cannot be employed, the observation was made on the surface of the sticking tape side by using binocular. As a result, a photocatalyst layer has not been slicked.

\* 4 : The determination of the light transmittance could not be made due to its abnormal configuration.

\* 5 : The determination of the light transmittance could not be made because of an opaque carrier.

[0125] In reference example 5, a structure, wherein a photocatalyst layer is carried but no adhesive layer is carried thereon, is disclosed. In this case, the photocatalyst layer has no adhesive property and is easily delaminated from the substrate, and it is observed that the surface of polyester film after receiving a durability test was deteriorated due to photocatalytic action, and the presence of holes and cracks were observed on the film through a binocular.

[0126] In examples 36 and 37, a structure, wherein acryl-silicon resin was used for forming an adhesive layer and a complex prepared and composed with 40-50% by weight of fine granule titanium dioxide P-25 manufactured by Nihon Aerozil Co., Ltd., 40% by weight of silica sol represented at (Z-1) and 10-20% by weight of acryl-silicon resin emulsion



was used for forming a photocatalyst layer, is disclosed. The structures disclosed in these examples were found to have good adhesive property after receiving boiling test as well as good durability and resistance against accelerated weathering.

[0127] In examples 38 through 42, a structure, wherein acryl-silicon resin containing polysiloxane was used for forming an adhesive layer and the same photocatalyst powder as the one used in the example 36 was used for forming a photocatalyst layer, and type and content of a sol for forming compoundable gel were changed, is disclosed. The structures prepared in these examples were found to have good photocatalytic activity as well as good adhesive property, durability and resistance against accelerated weathering after receiving boiling water test. In both cases that the resin whereinto polysiloxane was introduced was acryl-silicon resin containing 3% by weight of silicon (examples 38 and 39) or acryl-silicon resin containing 10% by weight of silicon (examples 40, 41 and 42), the adhesive property, durability and resistance against accelerated weathering of the structures were found to be excellent.

[0128] In examples 44 and 45, a structure, wherein an adhesive layer and a photocatalyst layer were carried on either polyethylene mesh or polypropylene tube, is disclosed, and the structures prepared in these examples were found to have good photocatalytic activity, adhesive property and durability.

[0129] Such good physical properties were also observed for the structures wherein the resin whereinto polysiloxane was introduced is any of epoxy-silicon resin (examples 43 and 46), polyester resin (example 44) and acryl resin (example 47).

[0130] However, as shown in reference example 6, a photocatalyst layer lost its adhesive property and was defoliated, when the content of polysiloxane in an adhesive layer became 70% by weight even though acryl-silicon resin containing polysiloxane was used for the adhesive layer.

[0131] In examples 48 through 53, a structure, wherein a resin containing colloidal silica was used for forming an adhesive layer, and the structures prepared in these examples were found to have good photocatalytic activity, adhesive property after receiving boiling water test, durability and resistance against accelerated weathering. In particular, the structures, wherein colloidal silica having fine particle diameter (KS-2) and acryl-silicon emulsion resin introduced with said colloidal silica were used (examples 50 through 53), were found to have excellent physical properties.

[0132] Whereas, the adhesive property and the durability of the structure, wherein the content of colloidal silica in the adhesive layer was increased to 50% by weight (reference example 7), was found to be radically deteriorated.

[0133] In examples 44 through 47, a structure, wherein an adhesive layer and a photocatalyst layer were provided by bar coat method, and a coating material for forming the photocatalyst layer was prepared by dispersing titania sol acidified with nitric acid and containing 12% by weight of titanium dioxide, which was replaced from fine granule titanium dioxide (P-25) manufactured by Nihon Aerosol Co., Ltd., silica gel (Trade name: Cataloid SI-30) manufactured by Shokubai Kasei Co., Ltd. and either alumina sol-200 manufactured by Nissan Chemical Industries Co., Ltd. or zirconia sol manufactured by Nippon Soda Co., Ltd., adjusting the pH of the resulting mixture to 1.5, and adding a predetermined amount of a surfactant to the said mixture. The structures prepared in these examples were found to have good adhesive property and durability as well as high photocatalytic activity even though the thickness of the photocatalytic layer is relatively thin.

[0134] In example 47, a structure having good physical properties was obtained even decreasing the content in total of acryl-silicon resin emulsion and silane coupler in a photocatalyst layer down to 20% by weight, however, in reference example 8, adhesive property and durability were radically decreased when such content in total was reduced down to 5% by weight even adding acryl-silicon resin emulsion to the photocatalyst layer.

[0135] The samples obtained in the examples 36 through 53 and allowed to all of a durability test under irradiation of black light at a high temperature and high humidity, dipping test in boiling water, and accelerated weathering test using Sunshine carbon arc weather meter, were checked again for their photocatalytic activity according to the same method employed at the start of this test based on decomposed-amount of acetaldehyde by light, and it is found that all samples showed the same decomposed-amount of acetaldehyde as the ones obtained at the start of this test and have maintained yet the initial photocatalytic activity with a full capacity.

#### Example 54

[0136] According to the method employed in the example 42, a sample of a titanium dioxide photocatalyst-carrying structure was prepared, and the antimicrobial activity of the sample was evaluated.

[0137] As a result, it was found that the survival rate of colon bacillus on the sample, which was left in a dark place, was 92%, 91% and 91% after 1, 2 and 3 hours, respectively, whereas such rate on the other sample, which was exposed to black light, was 52%, 22% and 11% after 1, 2 and 3 hours, respectively. The antimicrobial activity was noted even on the sample which was placed under a fluorescent lamp, and the survival rate of colon bacillus was 76%, 54% and 22% after 1, 2 and 3 hours, respectively, and those ratios were higher than the ones of the samples left in a dark place.

[0138] As a silicon compound used for a coating material of a photocatalyst, the followings were used.

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(S-1) 5% by weight ethanol solution of tetraethoxy silane (Super Reagent Grade, Manufactured by Wako Pure Chemical Co., Ltd.).

(S-2) 5% by weight ethanol solution of tetramethoxy silane (Manufactured by Shinetsu Chemical Industry Co., Ltd.

(S-3) 5% by weight ethanol solution of methyltriethoxy silane (Super Reagent Grade, Manufactured by Wako Pure Chemical Co., Ltd.).

(S-4) 5% by weight ethanol solution of tri( $\beta$ -methoxyethoxy)vinyl silane (Manufactured by Nihon Unicar Co., Ltd., Trade name: A-172).

[0139] To a sol solution and a silicon compound solution represented at (Z -1) through (Z-3), either titanium dioxide powder or sol was dispersed as a photocatalyst together with either water or a mixed solvent of water and ethanol while adjusting the pH of the mixture to an appropriate value ranging from 1.5 to 9 depending upon the type of raw materials and additives, and was further added with a prefixed amount of a surfactant to thereby obtain a coating material for forming a photocatalyst layer. The content of the components contained in the said coating material and viscosity and sedimentation state of the particles just after the preparation of the coating material and after 90 days from the sealing are presented in Table 6.

Table 6

	Photocatalyst		Metal Dioxide		Silicon Compound		At Start		After 90 days	
	Type	Content <sup>*1</sup>	Type	Content <sup>*1</sup>	Type	Content <sup>*1</sup>	Viscosity	Sedimentation	Viscosity	Sedimentation
Example		wt%		wt%		wt%	cP	%	cP	%
55	C-1	20	Z-1	20	S-1	1	31	100	43	90
56	C-1	10	Z-1	20	S-1	1	14	"	16	85
57	C-1	5	Z-1	5	S-1	0.2	3	"	4	95
58	C-2	30	Z-1	10	S-1	2	33	"	37	100
59	C-2	10	Z-1	10	S-3	0.1	7	"	9	100
			Z-2	0.3						
60	C-2	2	Z-1	2	S-3	0.01	1	"	1	100
			Z-2	0.05						
61	C-1	0.5	Z-1	0.5	S-2	0.02	1	"	1	95
62	C-1	0.1	Z-1	0.1	S-2	0.002	1	"	1	95
63	C-1	3	Z-1	6	S-1	0.2	2	"	2	90
	C-2	3	Z-3	0.2						
64	C-3	5	Z-1	7	S-4	0.2	3	"	5	95
65	C-3	1	Z-1	2	S-3	0.04	2	"	2	100
66	C-3	0.2	Z-1	0.2	S-1	0.01	1	"	1	100
Reference Example										
9	C-1	5	Z-1	5	-		3	100	12	45
10	C-2	30	Z-1	10	-		33	"	430	55
11	C-2	10	Z-1	10	-		7	"	23	65
			Z-2	0.3	-					
12	C-3	5	Z-1	7	-		3	"	9	50
13	C-3	1	Z-1	2	-		2	"	3	60

Note: Sedimentation of particles was indicated with a ratio of sedimentation volume relative to the whole volume of the coating solution.

\*1: The content is indicated with percent by weight based on the weight of dried coating solution.

[0140] In examples 55 through 57, a photocatalyst-carrying structure, wherein titanium dioxide powder (P-25) was used as a photocatalyst, is respectively disclosed. By the addition of a small amount of a silicon compound, the stability after 90 days of the coating material of a photocatalyst was improved very much.

[0141] In examples 58 through 60, titania sol acidified with nitric acid was used as a photocatalyst, silica gel and alumina sol were jointly used as the compoundable metal oxide sol, and methyltriethoxy silane was used as a silicon compound in examples 59 and 60. By employing this method, remarkable improvement in the resistant property to boiling water, particularly resistance to boiling water in tap water, of the structure formed with a film thereon by applying such coating material, was achieved.

[0142] In examples 61 and 62, a photocatalyst-carrying structure, wherein tetramethoxy silane was used as a silicon compound, and it is noted that this structure showed an advantage that it can keep the stability of the coating material, even the amount of tetramethoxy silane to add was so small.

[0143] In example 63, a photocatalyst-carrying structure, wherein powder titanium dioxide (P-25) and titania sol were jointly used for the photocatalyst, and silica sol and zirconia sol were jointly used for a compoundable metal oxide sol, is provided, whereas a coating material having good stability and sedimental property was obtained by adding tetramethoxy silane in the solution.

[0144] In examples 64 through 66, a photocatalyst-carrying structure, wherein a coating material for forming a photocatalyst layer was prepared by changing the type of silicon compounds, and each coating material prepared in these examples were found to be stable at any prefixed amount to add.

[0145] On the contrary, in examples 9 through 13, since no silicon compound was added to a coating material, the viscosity of the coating material was drastically increased after 90 days, and sedimentation of particles was certainly resulted in, and therefore, it was difficult to control the condition for forming films when such coating material was used, and it was not feasible to obtain a photocatalyst-carrying structure having stable quality.

( Examples 67 through 71 )

[0146] By using the coating materials prepared in the examples 55 through 59, photocatalyst-carrying structures were prepared by using the substrates recited in the following. The materials used for the substrate were as follows.

- (SA) Primer-treated polyester film
- (SB) Soda lime-made glass plate
- (SC) Metal aluminium plate
- (SD) High-density polyethylene mesh (Thickness of fiber: 0.2 mm, mesh size: 0.6 mm)
- (SE) Polypropylene-made mesh (Inner diameter: 30 mm, Outer diameter: 36 mm)

[0147] The adhesive layer was formed by dipping method when the thickness thereof was 2  $\mu\text{m}$  or less or the configuration of the substrate was other than plate-shaped, or by a method using a baker applicator when the substrate was plate-shaped and the thickness thereof was formed to 2  $\mu\text{m}$  or more. Temperature used for drying the adhesive layer was 80 °C only when the material of the substrate was (SD) or (SE), and it was at 120°C in all other cases. The photocatalyst layer was formed by dipping method when the thickness thereof was 2  $\mu\text{m}$  or less or the configuration of the substrate was other than plate-shaped, or by a method using a bar coator when the substrate was plate-shaped and the thickness thereof was formed to 2  $\mu\text{m}$  or more. Drying of the photocatalyst layer was performed at the same temperature as the one for drying the adhesive layer. Hereunder, physical properties of the photocatalyst-carrying structures prepared in the examples and the reference examples, wherein type and content of the materials described above, the thickness of a film coated, method to form films, etc. were each modified, are presented in Tables 7 and 8.

Table 7

Example	Carrier	Coating Solution for Adhesive Layer			Coating Solution for Photocatalyst Layer				Thick-ness of Adhesive Layer ( $\mu$ )	Thick-ness of Photocatalyst Layer ( $\mu$ )
		Type	Con- tent *1	Resin Sol.	TiO <sub>2</sub>		Z-1	Z-2		
					Type	Con- tent *2	Con- tent *2	Content *2		
Example-67	SA	PS-1	10	J-1	C-1	20	20	-	3	3
Example-68	SA	PS-1	5	J-1	C-1	2	0	-	1	3
Example-69	SC	PS-1	20	J-2	C-1	5	5	-	4	2
Example-70	SD	PS-2	20	J-2	C-2	30	10	-	5	3
Example-71	SE	PS-2	30	J-2	C-2	10	10	0.3	4	2

\* 1 : Concentration of solid component of the resin in the coating solution.

\* 2 : Concentration of solid component in the coating solution.

Table 8

Example	Photocatalytic Activity	Adhesive Property			Sunshine Weather Meter		Whole light Transmittance (%)
		Before Dura- bility Test	After Dura- bility Test	After Boiling Water Test	Surface State aft. Test	Adh. Pro. after Test	
Example-67	A	10	10	-* 6	A	10	63
Example-68	A	10	10	-* 6	A	10	75
Example-69	B	10	10	-* 6	A	10	-* 5
Example-70	B	10	10	-* 6	A	-* 3	-* 4
Example-71	B	10	10	10	A	10	82

\* 3 : Since cross-cut Scotch tape test could not be employed, the surface of the sticking tape was observed by using a binocular, however, no adhesion of the photocatalyst layer was observed.

\* 4 : The determination could not be made due to the difference in configuration.

\* 5 : The determination could not be made because of an opaque carrier.

\* 6 : No evaluation has been made.

[0148] For the samples obtained in the examples 67 through 71 and allowed to black light resistance test under a high temperature and high humidity, dipping test in boiling water and accelerated weathering test by using Sunshine carbon arc weather meter, photocatalytic activity was respectively determined again based on decomposed-amount of acetaldehyde by light that was the method employed for such determination before starting the tests described above. From the result that the same level of decomposed-amount of acetaldehyde as the ones obtained before allowing the sam-

ples to such tests above was obtained, it is demonstrated that the original photocatalytic activity has been fully maintained in the structures

#### Example 72

[0149] A photocatalyst-carrying structure comprising titanium dioxide was prepared according to the same method as described in the example 67, and an antimicrobial test was carried out for the structure according to the method described above. The survival rate of colon bacillus on the structure with no radiation of light was 92%, 91% and 91% after 1, 2 and 3 hours, respectively, whereas the survival rate on the structure which was exposed to radiation of black light was 52%, 29% and 11% after 1, 2 and 3 hours, respectively. Further, the survival rate of colon bacillus on the structure exposed to radiation of fluorescent lamp was 76%, 54% and 22% after 1, 2 and 3 hours, respectively, which showed higher antimicrobial activity than the structure placed in a dark site.

#### (Example 73) Films processed with sticker

[0150] A solution for forming an adhesive layer was prepared by mixing 30% by weight of polysiloxane (Manufactured by Colcoat Co., Ltd., Trade name: Methyl Silicate 51) based on the weight of acryl-silicon resin and 5% by weight of a curing agent (silane coupler) based on the weight of acryl-silicon resin to a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 25% by weight of acryl-silicon resin which contains 3% by weight of silicon, and was diluted with methyl ethyl ketone to adjust the concentration to 10% by weight on the solid component basis.

[0151] The diluted solution obtained was applied by gravure printing onto a polyester film (Trade name: Cosmoline 50  $\mu$ m) A4100 manufactured by Toyobo Co., Ltd. so as to form a film having a thickness of 1  $\mu$ m after drying by using a microgravure coater (width: 70 cm) manufactured by Yasui Seiki Co., Ltd. at a speed of 15 m/sec and at dry zone temperature of 13.

[0152] The polyester film whereon an adhesive layer was formed was then applied with a coating material for forming a photocatalyst layer, which was prepared by dispersing titania sol acidified with nitric acid containing 20% by weight of titanium dioxide as a photocatalyst into silica sol acidified with nitric acid containing 20% of silicon oxide in the presence of a surfactant, and then diluting the dispersion with a mixture of ion-exchanged water and ethanol (mixing ratio, 50:50) to a concentration of 10% by weight on the solid components basis, by gravure printing same as for the adhesive layer to thereby obtain a polyester film formed with a photocatalyst layer having dried-thickness of 1  $\mu$ m.

[0153] Next, to the surface of the photocatalyst-carrying structure comprising polyester film whereon a photocatalyst was not applied, a solution prepared by adding 5% by weight on the solid basis of a coating agent for blocking thermic rays, STS-500, manufactured by Sumitomo Osaka Cement Co., Ltd. into a commercially-available sticker was applied by employing gravure printing method. The film applied with the sticker was winded while laminating the film with polyethylene film (Pyrene film-OT 20  $\mu$ m) P-2161, manufactured by Toyobo Co., Ltd. at a process for drying and winding at the drying zone in the gravure printer, to thereby providing a sticking film.

[0154] This kind of films can be used for a sticking film for window glass for automobiles, home window glass, and window glass for medical facilities, and they are advantageously characterized from their properties, such as antimicrobial activity, soiling resistant property and deodorant property, as well as scattering-preventive films at breaking of glass.

#### Example 74 Plate glass

[0155] To a plate glass made of soda lime having thickness of 1 mm and cut into a piece with a dimension of 5 cm x 5cm, a solution prepared by mixing 30% by weight of polysiloxane (methyl silicate 51, manufactured by Colcoat Co., Ltd.) based on the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 25 % by weight of acryl-silicon resin which contains 3% by weight of silicon, was applied by using No. 7 bar coater and was dried at 100 °C for 60 min. to form an adhesive layer. After allowing the plate glass to cooling under an ambient temperature, a coating material for forming a photocatalyst layer was prepared by dispersing titania sol acidified with nitric acid containing 20% by weight of titanium dioxide into silica sol acidified with nitric acid containing 20% by weight of silicon oxide in the presence of a surfactant. The solution obtained was then applied onto the adhesive layer described above by using No. 7 bar coater as well, and was then dried for 60 min. at 100 °C to thereby obtain a photocatalyst-carrying glass plate (Sample No. 1).

#### Example 75 Glass Fiber Papers

[0156] The solution for forming an adhesive layer used in the example 74 was diluted with xylene-propanol solution (mixing ratio, 50:50) to obtain a concentration of 5% by weight on the solid component basis. A glass fiber paper, SAS-030 (weight: 30 g/m<sup>2</sup>) manufactured by Oribest Co., Ltd. was dipped in the diluted solution prepared as described above

and was then pulled out, allowed to stand and dried at 100 °C for 120 min. to form an adhesive layer on the surface of the said glass fiber paper. Then, the glass fiber paper where the adhesive layer was formed was dipped into a solution prepared by diluting the coating material for forming a photocatalyst layer used in the example 74 with ion-exchanged water to a concentration of 10% by weight, and was pulled out and dried at 100°C for 120 min. to obtain a photocatalyst-carrying glass fiber paper (Sample No. 2).

#### Example 76 Lens for Glasses

[0157] An adhesive layer was formed onto lens for glasses, PC pointal coat TC(+)1.00S 0. 00 65 mmØ manufactured by Nikon Corporation, by applying a solution prepared by admixing polysiloxane (Methyl Silicate 51 manufactured by Colcoat Co., Ltd.) 20% by weight based on the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 10% by weight of acryl-silicon resin which contains 3% by weight of silicon onto the lens according to dipping method as described in the example 75, and the coated-lens were dried at 100 °C for 20 min. After cooling the lens at an ambient temperature, a coating material for forming a photocatalyst layer was prepared by dispersing titania sol as a photocatalyst acidified with nitric acid and containing 5% by weight of titanium dioxide into silica sol acidified with nitric acid and containing 5% silicon oxide in the presence of a surfactant. Using this coating material for photocatalyst layer and employing dipping method similarly, a photocatalyst layer was formed by coating the said coating material onto the surface of said adhesive layer and was dried at 100 °C for 20 min. to obtain photocatalyst-carrying lens for glasses (Sample No. 3).

#### Example 77 Wall Papers made of Poly(vinyl chloride)

[0158] A solution prepared by mixing polysiloxane (Methyl Silicate 51 manufactured by Colcoat Co., Ltd.) 30% by weight based on the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 25% by weight of acryl-silicon resin which contains 3% by weight of silicon was applied onto a wall paper made of poly(vinyl chloride)(SG 5328, manufactured by Sangetsu Co., Ltd.) cut into a piece with a demension of 5 cm x 5 cm and a thickness of 1 mm by using a bar coater No. 7, and the applied-paper was then dried at 100 °C for 20 min. to obtain an adhesive layer. After cooling the paper at an ambient temperature, a coating material for forming a photocatalyst layer was prepared by dispersing titania sol as a photocatalyst acidified with nitric acid and containing 20% by weight of titanium dioxide into silica sol acidified with nitric acid and containing 20% silicon oxide in the presence of a surfactant. Applying this solution onto the surface of the adhesive layer by using a bar coater No. 7, and the paper coated was dried at 100 °C for 20 min. to obtain a photocatalyst-carrying wall paper (Sample No. 4).

#### Example 78 Polyester Films

[0159] The solution for forming an adhesive layer used in the example 77 was diluted with a mixed solution of xylene and isopropanol (mixing ratio, 50:50) to adjust the concentration of the mixture to 25% by weight on the solid components basis. The diluted solution was then applied by gravure printing at a speed of 10 m/min. and at dry zone temperature of 130 °C onto a polyester film (Cosmoshine) A4100 manufactured by Toyobo Co., Ltd. by using a microgravure coater (width: 70 cm) manufactured by Yasui Seiki Co., Ltd. to form a film with a thickness after drying of 3 µm. [0160] Then, the polyester film formed with an adhesive layer was further applied with the coating material for forming a photocatalyst layer used in the example 77 according to gravure printing to thereby obtain a photocatalyst-carrying polyester film provided with a photocatalyst layer having a thickness after drying of 3 µm (Sample No. 5).

#### Example 79 Protective Filters for Personal Computers

[0161] A solution for forming an adhesive layer was prepared by mixing polysiloxane (Methyl Silicate 51 manufactured by Colcoat Co., Ltd.) 30% by weight on the solid component basis relative to the weight of acryl-silicon resin into a xylene solution containing 20% by weight of acryl-silicon resin which contains 20% by weight of silicon and was diluted with an isopropanol solution to adjust the concentration to 20% by weight on the solid component basis. Then, the solution was applied by dipping onto VDT filter, E-filter III, manufactured by Toray Co., Ltd. and the filter coated was then dried at 100 °C for 20 min. to form an adhesive layer on the surface of the filter. Subsequently, the VDT protective filter formed with adhesive layer was further allowed to dipping process in a solution prepared by diluting the coating material used in the example 77 with ion-exchanged water to the extent that the content of solid component in the coating material to be 10% by weight, pulled out therefrom and dried at 100°C for 20 min. to obtain a photocatalyst-carrying VDT filter (Sample No. 6).

## Example 80 Telephone Set Cases

[0162] The solution for forming an adhesive layer used in the example 77 was diluted with a mixed solution of xylene and isopropanol (mixing ratio, 50:50) to adjust the concentration of the solution to 20% by weight on the solid component basis. The diluted-solution was applied by spraying to a case for a telephone set (Type: HIT-1, Manufactured by Hitachi Seisakusho Co., Ltd.) by using a spray gun (Type: WIDER 88 Manufactured by Iwata Tosoki Kogyo Co., Ltd.). After drying the sprayed-case at 100 °C for 20 min., a coating material for forming a photocatalyst layer used in the example 1 was adjusted by dilution with ion-exchanged water to a concentration of 8% by weight on the solid component basis, and the diluted-coating material was applied by spraying as described above. After drying the case at 100°C for 20 min., a photocatalyst-carrying telephone set case was obtained (Sample No. 7).

## Example 81 Lens for Glasses

[0163] An adhesive layer was formed onto lens for glasses, NL70HCCTc(+1.0 OS 0. 00 (70 mm $\phi$ ) manufactured by Nikon Corporation, by applying a solution prepared by admixing polysiloxane (Methyl Silicate 51 manufactured by Colcoat Co., Ltd.) 20% by weight based on the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 10% by weight of acryl-silicon resin which contains 3% by weight of silicon onto the lens according to dipping method as described in the example 79, and the coated-lens were dried at 100°C for 20 min. After cooling the lens at an ambient temperature, a coating material for forming a photocatalyst layer, which was prepared by dispersing titania sol as a photocatalyst acidified with nitric acid and containing 15% by weight of titanium dioxide into silica sol acidified with nitric acid and containing 15% silicon oxide in the presence of a surfactant, was applied onto the lens to form a photocatalyst layer. Using this solution for photocatalyst layer and employing the same dipping method, a photocatalyst layer was formed by coating the solution onto the surface of said adhesive layer and was dried at 100 °C for 20 min. to obtain photocatalyst-carrying lens for glasses (Sample No. 8).

## Example 82 Curtains

[0164] Textile fabrics for curtains, trade name "Hospia" (for school and hospital use) manufactured by Kawashima Orimono Co., Ltd. were cut into a piece with a dimension of 7 cm x 7 cm, and the pieces were dipped into a solution prepared by mixing polysiloxane (Methyl Silicate 51 manufactured by Colcoat Co., Ltd.) 20% by weight on the solid component basis relative to the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 15% by weight of epoxy-silicon resin which contains 3% by weight of silicon, pulled out therefrom and dried at 80 °C for 120 min. After cooling the fabrics at an ambient temperature, the textile fabrics whereto an adhesive layer was formed thereon was dipped into a coating material for forming photocatalyst layer which was prepared by dispersing titania sol produced by Ammonia Alkali containing 10% by weight of titanium dioxide into silica sol containing 10% by weight of silicon oxide in the presence of a surfactant, pulled out therefrom and dried at 80°C for 120 min. to obtain a photocatalyst-carrying textile fabric for curtain use (Sample No. 9).

## Example 83 Nonwoven Fabrics

[0165] Non-bleached nonwoven fabric made of cotton (Trade name: Orcos, Manufactured by Nishinbo Co., Ltd.) was cut into pieces each having a dimension of 7 cm x 7 cm, and each piece was sprayed with a solution prepared by mixing polysiloxane (Methyl Silicate 51 manufactured by Colcoat Co., Ltd.) 30% by weight based on the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 25% by weight of acryl-silicon resin which contains 3% by weight of silicon by using a spray gun (Type: WIDER 88, Manufactured by Iwata Tosoki Kogyo Co., Ltd.). After drying the sprayed fabric at 100 °C for 30 min., the solution for forming a photocatalyst layer used in the example 82 was applied to the said fabric, and the applied fabric was then dried at 100°C for 30 min. to obtain a photocatalyst-carrying cotton nonwoven fabric suitable for surgical gowns, tableclothes, covers for a toilet seat, shoji papers, covering sheets for seedlings, food packaging materials, etc.

## Example 84 Printed Polyester Cloth Fabrics for Umbrella

[0166] Using commercially available printed polyester cloth fabrics for umbrella use as a substrate, an adhesive layer and a photocatalyst layer were coated thereon according to the same method disclosed in the example 83. The photocatalyst-carrying printed polyester cloth fabric obtained here was found to have almost no difference in patterns and feeling from normal cloth fabrics (Sample No. 11).



## Example 85 Wall Papers (Woven Cloth)

[0167] Using a plain woven cloth, SG 6758, manufactured by Sangetsu Co., Ltd. as a substrate, an adhesive layer and a photocatalyst layer were formed onto the cloth according to the method disclosed in the example 83.

[0168] The photocatalyst-carrying woven cloth wall paper did not give bad influence on the quality of the woven cloth (Sample No. 2).

## Example 86 Aluminum Sash

[0169] A solution prepared by mixing polysiloxane (Methyl Silicate 51, manufactured by Colcoat Co., Ltd.) 30% by weight based on the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 25% by weight of acryl-silicon resin which contains 3% by weight of silicon was applied onto a aluminum sash plate cut into a piece with a dimension of 7 cm x 7 cm by using a bar coater No. 7 and the aluminum sash plate was dried at 100°C for 60 min. to form an adhesive layer on the plate. After cooling the plate at an ambient temperature, a coating material for forming a photocatalyst layer was prepared by dispersing titania sol acidified with nitric acid containing 20% by weight of titanium dioxide into silica sol acidified with nitric acid containing 20% by weight of silicon oxide in the presence of a surfactant. The coating material was then applied onto the surface of the adhesive layer described above by using a bar coater No. 7, and the applied plate was dried at 130°C for 10 min. to obtain a photocatalyst-carrying aluminum plate (Sample No. 13).

## Example 87 Stainless Steel Plates

[0170] The solution for forming an adhesive layer used in the example 86 was adjusted by dilution with a mixed solution of xylene and isopropanol (mixing ratio, 50:50) to a concentration of 5% by weight on the solid component basis. A stainless steel plate made of SUS 316 (Thickness: 0.2 mm) cut into a piece with a dimension of 7 cm x 7 cm was dipped into the solution described above, pulled out therefrom and dried at 120 °C for 20 min. to form an adhesive layer on the surface of the stainless steel plate. Then, the stainless steel plate where to an adhesive layer was formed was dipped into a solution prepared by adjusting the concentration of the coating material for a photocatalyst layer used in the example 86 with ion-exchanged water to a concentration of 10% by weight, pulled out therefrom and dried at 120 °C for 20 min. to obtain a photocatalyst-carrying stainless steel plate (Sample No. 14).

## Example 88 Tin Plates

[0171] A tin plate having a thickness of 1 mm cut into a piece with a dimension of 7 cm x 7 cm was dipped into a solution prepared by mixing polysiloxane (Methyl Silicate 51, manufactured by Colcoat Co., Ltd.) 30% by weight based on the weight of acryl-silicon resin into 20% by weight of xylene solution of acryl-silicon resin which contains 20% by weight of silicon and then diluting the mixture with isopropanol solution up to a concentration of 20% by weight on the solid component basis, pulled out therefrom and dried at 100°C for 60 min. to form an adhesive layer on the tin plate. The tin plate on which an adhesive layer was formed was then dipped into a solution prepared by adjusting the coating material for forming a photocatalyst layer used in the example 86 by dilution with ion -exchanged water to a concentration of 10% by weight, pulled out from the solution and dried at 100 °C for 60 min, to obtain a photocatalyst-carrying tin plate (Sample No. 15).

## Example 89 Blinds

[0172] After removing a slat having a width of 800 mm and a height of 700 mm of a blind, "Silky Curtain" (15 mm slat width type) T-12 (white), manufactured by Tachikawa Blind Industry Co., Ltd., a solution prepared by mixing polysiloxane (Methyl Silicate 51, manufactured by Colcoat Co., Ltd.) of 30% by weight based on the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 25% by weight of acryl-silicon resin which comprises 3% by weight of silicon was applied by spraying by using a spray gun, WIDER 88, manufactured by Iwata Tosoki Kogyo Co., Ltd. After drying the sprayed-blind at 120 °C for 20 min., the blind was further applied by spraying with a solution prepared by diluting the coating material for forming a photocatalyst layer used in the example 86 with ion-exchanged water to a concentration of 8% by weight on the solid component basis (Sample No. 16).

## Example 90 Printed Plywood

[0173] A printed plywood, Neowood, having a thickness of 2.5 mm and cut into a piece with a dimension of 7 cm x 7 cm, manufactured by Eidai Sangyo Co., Ltd. was applied with a solution prepared by mixing polysiloxane (Methyl Sil-

cate 51, manufactured by Colcoat Co., Ltd.) 30% by weight based on the weight of acryl-silicon resin into a mixed solution of xylene and isopropanol (mixing ratio, 50:50) containing 25% by weight of acryl-silicon resin which comprises 3% by weight of silicon by using a bar coater No. 7 and was then dried at 100 °C for 30 min. to form an adhesive layer on the printed plywood. After cooling the printed plywood at an ambient temperature, a coating material for forming a photocatalyst layer was prepared by dispersing titania sol acidified with nitric acid containing 20% by weight of titanium dioxide into silica sol acidified with nitric acid containing 20% silicon oxide in the presence of a surfactant. Using this coating material and a bar coater No. 7, the coating material was applied on the surface of the adhesive layer and was dried at 100 °C for 30 min. to obtain a photocatalyst-carrying printed plywood (Sample No. 17).

#### Example 91 Synthetic Timbers

[0174] The solution for forming an adhesive layer used in the example 90 was diluted with a mixed solution of xylene and isopropanol (mixing ratio, 50:50) to a concentration of 5% by weight on the solid component basis.

[0175] A synthetic timber, Eson Neolamber FFU-50, manufactured by Sekisui Chemical Industry Co., Ltd. and cut into a piece with a dimension of 7 cm x 7 cm was dipped into the diluted solution prepared above, pulled out therefrom and dried at 100 °C for 120 min. to form an adhesive layer on the surface of the timber. The timber on which the adhesive layer was formed was then dipped into a solution prepared by diluting the coating material for forming a photocatalyst layer used in the example 90 with ion-exchanged water to a concentration of 10% by weight, pulled out therefrom and dried at 100°C for 120 min. to obtain a photocatalyst-carrying synthetic timber (Sample No. 18).

#### Example 92 Wooden Doors

[0176] An indoor use wooden door (Type 38 RC0202-IR6, Oak pattern) manufactured by Daiken Kogyo Co., Ltd. was cut into a piece with a dimension of 7 cm x 7 cm, and the piece was applied with a solution prepared by mixing polysiloxane (Methyl Silicate 51, manufactured by Colcoat Co., Ltd.) 20% by weight based on the weight of acryl-silicon resin (mixing ratio, 50:50) containing 10% by weight of acryl-silicon resin which comprises 3% by weight of silicon according to the dipping method similar to the one as described in the example 91 to form an adhesive layer and was dried at 100°C for 20 min. After cooling the piece at an ambient temperature, a coating material for forming a photocatalyst layer was prepared by dispersing titania sol acidified with nitric acid containing 5% by weight of titanium dioxide into silica sol acidified with nitric acid containing 5% by weight of silicon oxide in the presence of a surfactant. This coating material was applied onto the surface of the adhesive layer by employing the dipping method described above and dried at 100 °C for 20 min. to obtain a photocatalyst-carrying wooden door.

(Evaluation for Photocatalytic Activity)

[0177] Photocatalytic activity of the samples 1 through 19 was evaluated respectively, and the results in the evaluation were presented in Table 9.

Table 9

	Total Ray Transmissibility	Aldehyde Decomposing Activity	Salad Oil Decomposing Activity	Antimicrobial Activity	Initial Adhesive Property	Durability
Sample 1	85 %	A	A	A	10 Points	10 pt
Sample 2	65	B	A	-	5% or less weight reduction by 10 min. ultra-sonification	Same as Initial Adhesive Property
Sample 3	90	B	B	A	10	10
Sample 4	-	B	A	A	10	10
Sample 5	90	A	A	A	10	10
Sample 6	-	B	A	A	10	10
Sample 7	-	B	A	A	10	10
Sample 8	95	B	B	A	10	10
Sample 9	- %	A	A	A	* 1	* 1
Sample 10	-	A	A	A	* 1	* 1
Sample 11	-	B	A	A	* 1	* 1
Sample 12	-	B	A	A	* 1	* 1
Sample 13	-	A	A	A	10	10
Sample 14	-	B	A	A	10	10
Sample 15	-	A	A	A	10	10
Sample 16	-	B	A	B	8	8
Sample 17	-	B	A	A	8	8
Sample 18	-	A	A	A	10	10
Sample 19	-	A	A	A	10	10

\* 1 : Since basic grain tape method could not be employed, the surface of the sticking tape was observed, however, no adhesion of the photocatalyst layer was recognized.

#### Industrial Use

[0178] The photocatalyst-carrying structure according to the present invention has high photocatalytic activity, and glass, plastics, metallic materials, cloth fabrics, timbers and wooden materials, which respectively carry a photocatalyst being resistant to deterioration and highly durable, can be useful for lens, various types of window glass, adhesive films, sheets for decoration, wall papers, curtains, construction materials, such as blinds, interior goods, etc.

#### Claims

1. A photocatalyst-carrying structure constituted with a photocatalyst layer, an adhesive layer and a substrate, wherein the adhesive layer is provided in between the photocatalyst layer and the substrate and is made of silicon-modified resin containing silicon from 2 to 60% by weight, a resin containing colloidal silica from 5 to 40% by weight, or a resin containing polysiloxane, which is a polycondensation product of a compound represented by a formula (1),



wherein  $R^1$  is an alkyl having 1-8 carbon atoms and optionally substituted with any of amino, carboxyl or chlorine atom,  $R^2$  is an alkyl having 1-8 carbon atoms or an alkoxy-substituted alkyl having 1-8 carbon atoms,  $n_1$  is an integer, 0, 1 or 2,  $n_2$  and  $n_3$  are each independently an integer, 0, 1, 2 or 3,  $n_4$  is an integer, 2, 3 or 4, and  $n_1 + n_2 + n_3 + n_4 = 4$ , from 3 to 60% by weight, and the photocatalyst layer is made of a photocatalyst particle complex containing either a metal oxide gel or a metal hydroxide gel from 25 to 95% by weight.

2. The photocatalyst-carrying structure according to claim 1, where in the silicon-modified resin used for the adhesive layer is acryl-silicon resin.
3. The photocatalyst-carrying structure according to claim 1, where in the adhesive layer is composed of a resin containing polysiloxane, and said polysiloxane is made of either a hydrolyzed product of silicon alkoxide containing at least one  $C_1$ - $C_5$  alkoxy or a compound prepared via the said hydrolyzed product.
4. The photocatalyst-carrying structure according to any of claims 1 to 3, wherein the adhesive layer is made of silicon-modified resin containing polysiloxane.
5. The photocatalyst-carrying structure according to claim 1, where in the adhesive layer is made of a resin containing colloidal silica and the diameter of the particles of the colloidal silica is 10 nm or less.
6. The photocatalyst-carrying structure according to any of claims 1, 2 or 5, wherein the adhesive layer is made of silicon-modified resin containing colloidal silica.
7. The photocatalyst-carrying structure according to any of claims 1 to 6, wherein the metal oxide gel or the metal hydroxide gel contained in the photocatalyst layer is porous gel and their specific surface are dried at 150°C is 100  $m^2/g$  or more, and is composed of one or more gels of metals selected from a group consisting of silicon, aluminum, titanium, zirconium, magnesium, niobium, tantalum, tungsten and tin, respectively.
8. The photocatalyst-carrying structure according to any of claims 1 to 7, wherein the photocatalyst layer is a photocatalyst complex composed of more than 2 kinds of metal oxide gels or metal hydroxide gels and a photocatalyst, and the adhesive property of the complex after dipping it into boiling water which shows an electroconductivity of 200  $\mu S/cm$  at 20°C is expressed as an evaluated-point of 6 or more according to cross-cut Scotch tape test provided in JIS K5400.
9. The photocatalyst-carrying structure according to claim 8, where in the photocatalyst layer is composed of a photocatalyst complex, which comprises porous oxide gel or hydroxide gel of one or more metals selected from a group consisting of aluminum, titanium, zirconium and niobium, and silicon, and has a specific surface area after drying at 150 °C of 50  $m^2/g$  or more.
10. The photocatalyst-carrying structure according to any of claims 1 to 7, wherein the photocatalyst layer is composed of a photocatalyst complex which contains either silicon-modified resin or silane compound 10 to 50% by weight, either a metal oxide gel or a metal hydroxide gel from 15 to 85 % by weight on the solid component basis and a photocatalyst from 5 to 75% by weight, and the photocatalyst complex has an adhesive property of point 6 or more expressed from the criterion according to cross-cut Scotch tape test provided in JIS K5400 after dipping it for 15 min. into boiling water which shows an electroconductivity of 200  $\mu S/cm$  at 20°C.
11. The photocatalyst-carrying structure according to claim 10, wherein the silicon-modified resin or the silane compound contained in the photocatalyst layer is acryl-silicon resin, epoxy-silicon resin or a silane coupler.
12. The photocatalyst-carrying structure according to any of claims 1 to 11, wherein the thickness of the adhesive layer is 0.1  $\mu m$  or more.
13. The photocatalyst-carrying structure according to any of claims 1 to 12, wherein the thickness of the photocatalyst layer is 0.1  $\mu m$  or more.
14. The photocatalyst-carrying structure according to any of claims 1 to 13, wherein whole light transmittance through both adhesive layer and photocatalyst layer at a wavelength of 550 nm is 70% or more.
15. The photocatalyst-carrying structure according to any of claims 1 to 14, characterized in that the adhesive property

of the structure after exposing it to black light radiation of which ultraviolet light intensity is 3 mW/cm<sup>2</sup> for 500 hours at 40°C and 90% R.H. is evaluated as point 6 or more according to the criterion of cross-cut Scotch tape test provided in JIS K5400.

- 5 16. A photocatalyst-carrying glass, characterized in that the glass has a constitution wherein an adhesive layer is provided in between a photocatalyst layer and a substrate, and the adhesive layer and the photocatalyst layer described in any of the claims 1 to 15 are used therein.
- 10 17. The photocatalyst-carrying glass according to claim 16, characterized in that the configuration of the carrier is any of plate-shaped, tubular, ball-shaped or fiber-like.
18. An interior goods using at least partly the photocatalyst-carrying glass described in claim 16 or 17.
- 15 19. Glasses and glass lens for which the photocatalyst-carrying glass described in claim 16 or 17 is used.
- 20 20. A photocatalyst-carrying plastic molding which has a structure wherein an adhesive layer is provided in between a photocatalyst layer and a plastic molding, and the photocatalyst layer and the adhesive layer used therein are the ones described in any of claims 1 through 15.
- 25 21. The photocatalyst-carrying plastic molding according to claim 20, characterized in that the configuration of the molding is plate-shaped, tubular, ball-shaped, fiber-like or film-like.
22. A construction material at least partly using the photocatalyst-carrying plastic molding described in claim 20 or 21.
- 30 23. An interior goods at least partly using the photocatalyst-carrying plastic molding described in claim 20 or 21.
24. An electric appliance at least partly using the photocatalyst-carrying plastic molding described in claim 20 or 21.
- 35 25. A furniture at least partly using the photocatalyst-carrying plastic molding described in claim 20 or 21.
26. A toy at least partly using the photocatalyst-carrying plastic molding described in claim 20 or 21.
27. A sticking film prepared by applying a sticker onto the back side of the photocatalyst-carrying plastic film described in claim 20 or 21.
- 40 28. A photocatalyst-carrying cloth which has a structure wherein an adhesive layer is provided in between a photocatalyst layer and a substrate, and the photocatalyst layer and the adhesive layer used therein are the ones described in any of claims 1 through 13 and 15.
29. A furniture and a household goods at least partly using the photocatalyst-carrying cloth described in claim 28.
30. An interior goods at least partly using the photocatalyst-carrying cloth described in claim 28.
- 45 31. A toy at least partly using the photocatalyst-carrying cloth described in claim 28.
32. A photocatalyst-carrying metal which has a structure wherein an adhesive layer is provided in between a photocatalyst layer and the metal, and the photocatalyst layer and the adhesive layer used therein are the ones described in any of claims 1 through 13 and 15.
- 50 33. The photocatalyst-carrying metal according to claim 32, characterized in that the configuration of the substrate is plate-shaped, tubular, ball-shaped, fiber-like or sheet-shaped.
34. A construction material at least partly using the photocatalyst-carrying metal described in claim 32 or 33.
- 55 35. An interior goods at least partly using the photocatalyst-carrying metal described in claim 32 or 33.
36. A sash using the photocatalyst-carrying metal described in claim 32 or 33.

37. A blind using the photocatalyst-carrying metal described in claim 32 or 33.
38. A photocatalyst-carrying timber and a photocatalyst-carrying wooden material which respectively has a structure wherein an adhesive layer is provided in between a photocatalyst layer and the timber or the wooden material, and the photocatalyst layer and the adhesive layer used therein are the ones described in any of claims 1 through 13 and 15.
39. The photocatalyst-carrying timber and the photocatalyst-carrying wooden material according to claim 38, characterized in that the configuration of the substrate is plate-shaped, columnar, ball-shaped or sheet-shaped.
40. An interior decoration material at least partly using the photocatalyst-carrying timber and the photocatalyst-carrying wooden material described in claim 38 or 39.
41. An interior goods at least partly using the photocatalyst-carrying timber and the photocatalyst-carrying wooden material described in claim 38 or 39.
42. A woodwork product using the photocatalyst-carrying timber and the photocatalyst-carrying wooden material described in claim 38 or 39.
43. A furniture using the photocatalyst-carrying timber and the photocatalyst-carrying wooden material described in claim 38 or 39.
44. A coating material of a photocatalyst comprising silicon compound from 0.001 to 5% by weight, a metal oxide sol and/or a metal hydroxide sol from 0.1 to 30% by weight on the solid component basis and a photocatalyst powder and/or sol from 0.1 to 30% by weight on the solid component basis.
45. The coating material of a photocatalyst according to claim 44, wherein the silicon compound is an alkoxy silane compound represented by a general formula (2),  $\text{SiR}^3\text{n}_5\text{)}_4\text{-n}_5 \cdot \cdot \cdot (2)$ , wherein  $\text{R}^3$  is an alkyl having 1-8 carbon atoms optionally substituted with amino, chlorine atom or carboxy,  $\text{R}^4$  is alkyl having 1-8 carbon atoms or alkoxy-substituted alkyl having 1-8 carbon atoms, and  $\text{n}_5$  is 0, 1, 2 or 3, or one or more of the hydrolyzed products of the such compound.
46. The coating material of a photocatalyst according to claim 44, characterized in that the metal oxide sol and/or the metal hydroxide sol comprise a metal selected from a group consisting of silicon, aluminium, titanium, zirconium, niobium, tantalum, magnesium, tungsten and tin, and the specific surface area of such sol after drying at 150°C is 50m<sup>2</sup>/g or more, respectively.
47. The coating material of a photocatalyst according to claim 44, characterized in that the silicon compound is composed of one or more compounds selected from a group consisting of tetramethoxy silane, tetraethoxy silane, methyl trimethoxy silane, methyl triethoxy silane and their hydrolyzed products.
48. A coating material of a photocatalyst used for producing a photocatalyst-carrying structure wherein an adhesive layer is provided in between a photocatalyst layer and a substrate and comprises two types of coating materials, those are (1) a coating material for forming an adhesive layer onto a substrate comprises a resin from 1 to 50% by weight which contains silicon-modified resin containing 2-60% by weight of silicon and either a resin containing 3-60% by weight of polysiloxane or a resin containing 5-40% by weight of colloidal silica, and (2) a coating material for forming a photocatalyst layer onto the adhesive layer comprise 0.001-5% by weight of a silicon compound, 0.1-30% by weight of a metal oxide sol and/or a metal hydroxide sol on the solid component basis and 0.1-30% by weight of a photocatalyst powder and/or sol on the solid component basis.
49. The coating material of a photocatalyst according to claim 48, wherein the resin contained in the coating material for forming an adhesive layer is a resin containing polysiloxane, and said polysiloxane is the hydrolyzed product of alkoxy silane with an alkoxy group having 1-5 carbon atoms or an other compound produced from said hydrolyzed product.
50. The coating material of a photocatalyst according to claim 48, wherein the resin contained in the coating material for forming an adhesive layer is a resin containing colloidal silica, and the diameter of said colloidal silica is 10 nm or less.

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51. The coating material of a photocatalyst according to claim 48, wherein the resin contained in the coating material for forming an adhesive layer is silicon-modified resin containing polysiloxane.

5 52. The coating material of a photocatalyst according to claim 48, wherein the resin contained in the coating material for forming an adhesive layer is silicon-modified resin containing colloidal silica.

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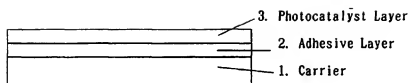
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Fig. 1





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/01669

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int. Cl <sup>6</sup> B01J35/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int. Cl <sup>6</sup> B01J35/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926 - 1996 Kokai Jitsuyo Shinan Koho 1971 - 1996		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 7-232080, A (TOTO Ltd.), September 5, 1995 (05. 09. 95), Claim; page 4, column 6, lines 30 to 45; page 5, column 7, lines 6 to 25 (Family: none)	1, 7, 12, 13, 16, 32, 33, 38-40, 43
A	JP, 4-307066, A (TOTO Ltd.), October 29, 1992 (29. 10. 92), Claim 1; page 2, column 2, lines 10 to 19 (Family: none)	16-18, 21, 23, 40, 41
A	JP, 7-168001, A (Nikon Corp.), July 4, 1995 (04. 07. 95), Page 3, column 4, lines 8 to 12 (Family: none)	19
A	JP, 6-315614, A (Director General, Agency of Industrial Science and Technology), November 15, 1994 (15. 11. 94), Claim 3; page 5, column 7, lines 19 to 33 & EP, 614682, A1	22, 34
A	JP, 8-7643, A (Mitsui Mining & Smelting Co.,	24, 35
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understate the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step unless the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Ltd.), January 12, 1996 (12. 01. 96), Claim 1; page 2, column 2, lines 26 to 33 (Family: none)	
A	JP, 8-74171, A (Komatsu Seiren Co., Ltd.), March 19, 1996 (19. 03. 96), Claim 1; page 2, column 2, lines 14 to 18 (Family: none)	38 - 30
A	JP, 8-131842, A (TOTO Ltd.), May 28, 1996 (28. 05. 96), Claim 6; page 5, column 7, lines 10 to 19 & EP, 684075, A1	44, 46

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(54) 発明の名称 固定化光触媒とその製造方法および有害物質の分解・除去方法

(57) 【要約】

【課題】光触媒反応効率が高く、固体表面の汚れ(汚れ付着物質)や、大気中あるいは水中の有害物質の分解等に対して優れた効果を示す固定化光触媒とその製造方法およびその光触媒を用いた有害物質の分解・除去方法を提供する。

【解決手段】平均結晶子サイズが5〜30 nmのアナタース型の結晶からなる二酸化チタンが基材表面に薄膜状に固定されている固定化光触媒。この固定化光触媒に有害物質を接触させた状態で高エネルギーの光を照射すれば有害物質の分解・除去に効果的である。この固定化光触媒は、チタニアゾルを基材に塗布した後、所定の焼成温度(250〜800℃)まで加熱し、その温度で短時間(30分以内)保持する焼成処理を施すことにより製造することができる。二酸化ジルコニウムおよび/またはジルコニウム塩を所定量添加したチタニアゾルを用いれば、焼成条件を緩和することができる。

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【特許請求の範囲】

【請求項1】平均結晶サイズが5～30nmのアナターズ型二酸化チタンが基材表面に薄膜状に固定されていることを特徴とする光触媒。

【請求項2】基材にチタニアゾルを塗布した後、250～800℃まで加熱し、その温度で30分以内保持する焼成処理を施すことを特徴とする請求項1に記載の固定化光触媒の製造方法。

【請求項3】Zr/Ti（モル比）が0.3未満となるように二酸化ジルコニウムおよびジルコニウム塩のいずれか一方または両方が添加されたチタニアゾルを基材に塗布した後、300～1000℃で焼成処理を施すことを特徴とする請求項1に記載の固定化光触媒の製造方法。

【請求項4】請求項1に記載の固定化光触媒と有害物質とが接触した条件下で前記固定化光触媒にバンドギャップ以上のエネルギーの光を照射することを特徴とする有害物質の分解・除去方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、防臭、防汚（固体表面の汚れ防止）、殺菌等に効果があり、大気汚染物質、あるいは排水中の汚染物質等の有害物質を分解・除去する作用を有し、さらには光電気化学、有機合成等への応用が可能な固定化光触媒とその製造方法およびその光触媒を用いる有害物質の分解・除去方法に関する。

【0002】

【従来の技術】半導体に光を照射すると、その照射面に強い還元作用を有する電子と強い酸化作用を有する正孔が生じ、半導体に接触した分子はその酸化還元作用によって分解される。

【0003】近年、半導体のこのような作用、すなわち光触媒作用を、NO<sub>x</sub>等の大気汚染物質の分解、防臭、防汚、殺菌、水の浄化等の様々な環境浄化技術に応用する試みが精力的に行われている。しかし、現状では光触媒反応の効率が悪く、実用化されている例は極めて少ない。

【0004】半導体光触媒は、従来から、粉末状で溶液中に懸濁させた状態、あるいは基材上に薄膜状に固定した状態で使用されてきた。光触媒の活性を高く維持するという観点から表面積の大きい微細な状態での使用が望ましいが、実用面からは、取り扱いが容易で、幅広い応用性を有する固定した状態で使用の方がはるかに有望といえる。

【0005】そのため、光触媒作用を有する半導体を基材に固定した光触媒（以下、これを「固定化光触媒」という）の活性を高める様々な方法が提案されてきた。例えば、特開平7-100378号公報には、アナターズ型の結晶からなる二酸化チタン固定化光触媒が開示されている。この光触媒は、基材上への塗布に用いる二酸化

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チタンのゾルにアルコールアミンを添加し、600～700℃の焼成温度までゆっくりと加熱昇温することにより製造される。しかしながら、この固定化光触媒では十分な光触媒活性が得られず、アルコールアミンが吸着しにくいため、製造時に多量のエネルギーを要するという問題もある。

【0006】また、特開平6-293519号公報には、塗布に用いるチタニアゾルをあらかじめ水熱処理することによって、それに含まれる二酸化チタンの微粒子を結晶成長させる固定化光触媒の製造方法が開示されている。この光触媒は比較的高い光触媒活性を有しているが、結晶成長したチタニアゾルは基材に均一に塗布されにくく、焼成後剥離しやすいという問題がある。さらに、水熱処理は高温、高圧下での反応であるとともに、反応速度、温度、圧力等に厳格なコントロールを要するため、光触媒の生産には適していない。

【0007】

【発明が解決しようとする課題】本発明は、上述したような状況下において、光触媒反応効率が高く、かつ、防臭、防汚、抗菌、および大気中あるいは排水中に含まれる有害物質（例えば、NO<sub>x</sub>、農薬、有機ハロゲン化合物等）の分解、無害化などに対して優れた効果を示し、かつ、経済性、安定性、安全性などの面からも好適な固定化光触媒とその製造方法、およびその光触媒を用いる有害物質の分解・除去方法を提供することを課題としてきたものである。

【0008】

【課題を解決するための手段】本発明者は、二酸化チタンを用いた、高い反応効率を示す固定化光触媒を開発すべく検討を重ねた結果、チタニアゾルを基材に塗布した後、焼成し、結晶成長させることにより、平均結晶サイズが5～30nmのアナターズ型二酸化チタンとすることができ、固定化された二酸化チタンの表面積が増大し、また、配位不飽和点、格子欠陥等の反応活性サイトが増加し、さらには、量子サイズ効果発現時には酸化還元力の増大効果も加わることによって、光触媒活性が著しく向上することを見出した。

【0009】また、このような特性を有する固定化光触媒は、基材表面にチタニアゾルを塗布した後、焼成を短時間とすることによって製造することができ、さらに、塗布に用いるチタニアゾルに所望量の二酸化ジルコニウムまたはジルコニウムの塩を添加することによって、一層容易に製造することが可能であることを知見した。

【0010】本発明はこれらの知見に基づきなされたもので、その要旨は、下記（1）の固定化光触媒、（2）および（3）のその製造方法、ならびに（4）のその固定化光触媒を用いる有害物質の分解・除去方法にある。

【0011】（1）平均結晶サイズが5～30nmのアナターズ型二酸化チタンが基材表面に薄膜状に固定されていることを特徴とする光触媒。

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【0012】(2) 基材にチタニアゾルを塗布した後、  
250～800℃まで加熱し、その温度で30分以内保  
持する焼成処理を施すことを特徴とする上記(1)に記  
載の固定化光触媒の製造方法。

【0013】(3)  $2r/\sqrt{t}$  (モル比)が0.3未満  
となるように二酸化ジルコニウムおよびジルコニウム  
のいずれか一方または両方が添加されたチタニアゾルを  
基材に塗布した後、300～1600℃で焼成処理を施  
すことを特徴とする上記(1)に記載の固定化光触媒の  
製造方法。

【0014】(4) 上記(1)に記載の固定化光触媒と  
有害物質とが接触した条件下で前記固定化光触媒にバ  
ンドギャップ以上のエネルギーの光を照射することを特  
徴とする有害物質の分解・除去方法。

【0015】前記「平均結晶サイズ」とは、基本的  
には透過型電子顕微鏡で直接観察した結晶粒径を意味す  
るが、この値は、X線回折によるアナタース( $d_{111}$ )  
のピークからScherrerの式を用いて算出した結晶  
サイズと良く一致することから、本発明では、平均  
結晶サイズとしてこれらいずれの値を採用してもよ  
い。なお、「平均」に特別な意味(限定)はなく、5 n  
m未満のもの、あるいは30 nmを若干超えるものか  
あったとしても、複数の結晶サイズの算術平均が5～3  
0 nmの範囲内であればよい。

【0016】

【発明の夜換の形態】以下、本発明、上記(1)～  
(4)の発明について詳細に説明する。

【0017】上記(1)の発明は、チタニアゾルを基材  
表面に塗布した後、焼成により薄層状の二酸化チタンを  
結晶成長させた結果得られるもので、その結晶サイズが  
平均で5～30 nmの範囲内にあることを特徴とする  
固定化光触媒(これを、「本発明の固定化光触媒」とい  
う)である。

【0018】本発明の固定化光触媒においては、まず、  
二酸化チタンの結晶構造がアナタース型でなければなら  
ない。後述する実施例で示すように、アナタース型で  
なければ光触媒活性の高い光触媒が得られないからで  
ある。

【0019】さらに、その平均結晶サイズ(以下、単  
に「結晶サイズ」という)が5～30 nmの範囲内に  
あることが必要である。結晶サイズが5 nm未満であ  
るということは、チタニアゾルに含まれる二酸化チタ  
ンの平均粒径が5 nm程度であることであって、そのよ  
うな微細の二酸化チタンを製造することは実質的に困難  
である。一方、結晶サイズが30 nmを超えると、光  
触媒活性が著しく低下する。

【0020】二酸化チタンを固定する基材としては、ス  
テンレス鋼、炭素鋼、亜鉛等のめっきを施した鋼板、あ  
るいはアルミニウム板、チタン板等の高純度の金属材料  
や、セラミックス、陶磁器、ガラス等の無機材料、樹

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脂、木材、活性炭等の有機材料から選択される任意の材  
料、あるいはその中の2種以上からなる複合材料など、  
広範囲にわたる材料が使用できる。既に塗布が施され  
ている部材を用いることもできる。また、基材の形状につ  
いても何等限定はなく、厚板、薄板などの板状、ビーズ  
のような球状、あるいはそのまま製品として供される複  
雑な形状であってもよい。また、表面が多孔質でも緻密  
質でもよい。

【0021】二酸化チタンの膜厚について特に限定はな  
い。一般に、厚くなるほど高い光触媒活性を示す傾向が  
ある。しかし、膜厚が2 μmを超えると光触媒活性の向  
上効果が認められず、膜の割れなどが起こりやすくなる  
ので、2 μm以下であることが好ましい。

【0022】この固定化光触媒は、太陽光や蛍光灯、プ  
ラックライト、水銀灯、キセノン灯等からの光によっ  
て、光触媒作用を発現し、消臭、防臭、防汚、ならび  
に大気中あるいは排水などに含まれる有害物質等の分解、  
無害化等に対して優れた効果を示す。また、この固定化  
光触媒は、安定性、安全性(毒性がない)などにも優れ  
ており、内装材、塗材、ガラス、化粧板、タイル等と  
して好適に利用でき、使用するに際し何等エネルギーを必  
要とせず(省エネルギー)、メンテナンスフリーである  
という利点も有している。

【0023】前記(2)の発明は上記(1)の固定化光  
触媒の製造方法で、チタニアゾルを基材に塗布した後、  
250～800℃(焼成温度)まで加熱し、その温度で  
短時間(30分以内)保持する焼成処理を施す方法であ  
る。

【0024】チタニアゾルの調製は、超微粒の二酸化チ  
タン(5～10 nm)を水に懸濁させた後、チタントラ  
マトキシド、チタントラマトキシド、チタントラ  
ノ-プロボキシド、チタントラノ-プロボキシ  
ド、チタントラノ-プロボキシド等のチタントラ  
ノコキシドや、チタノセチルセトネート、四塩化チ  
タン等を加水分解することによって行うことができる。  
また、ゾルには、ジエタノールアミン、トリエタノール  
アミン等のアルコールアミン類や、1,3-プロパンジオ  
ール等の軟溶媒添加してもよい。

【0025】このようにして得られたチタニアゾルに含  
まれる二酸化チタンの平均粒径は5～10 nm程度で  
あり、これを基材表面に塗布し、焼成し、結晶成長させ  
ることによって所望の結晶サイズ(5～30 nm)の  
二酸化チタン固定化光触媒とする。

【0026】基材へのチタニアゾルの塗布は、スピン  
コティング、ディップコティング、スプレーコーテ  
ィング、バーコートイング等によって行うことができる。

【0027】チタニアゾルを基材に塗布した後、焼成す  
ることによって固定化光触媒が得られるが、基材表面に  
薄層状に固定化した二酸化チタン等の無機酸化物の焼成は  
極めて速やかに起こり、結晶性が大きくなるため、通

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草の焼成条件では、上述した結晶子サイズが5〜30 nmの範囲にある二酸化チタンからなる本発明の固定化光触媒は得られない。

【0028】そこで、焼成を前記の所定の条件で行う。すなわち、チタニアゾルを基材に塗布した後、焼成温度まで加熱し、その温度で所定時間保持した後、冷却する焼成処理を行う。焼成は、塗布した状態（塗布状態）のまま行ってもよいし、あるいは塗布後100℃前後で乾燥した状態から行ってもよい。

【0029】焼成温度は250〜800℃の温度域とする。焼成温度が250℃より低いと二酸化チタンはアモルファスのままであり、一方、800℃を超えると結晶粒が成長して大きくなりすぎ、あるいはルチル晶が現れ、高い光触媒活性を有する固定化光触媒は得られない。

【0030】焼成温度までの加熱は急速に行うことが好ましい。加熱が急速に行われない場合は、前記の焼成温度に達するまでに二酸化チタンの凝結が進み過ぎ、結晶粒が粗大化する場合がある。好ましい加熱速度は、30℃/分以下である。なお、急速に加熱するには、熱処理炉をあらかじめ所定の温度に加熱しておき、その中へチタニアゾルを塗布した基材を直接投入する方法を用いるのが好適である。

【0031】焼成温度に達した後の保持時間（焼成時間）は30分以内とする。焼成温度に幅があるので、実際には、焼成温度として前記の温度範囲内の低めの温度に設定した場合は焼成時間を長くし、高めの温度に設定した場合は短くする等、適宜調節する。なお、焼成温度を400〜700℃の範囲とし、焼成時間を10分以内とするのが、高い光触媒活性を有する固定化光触媒を得る上で好ましい。

【0032】焼成後は冷却するが、冷却も急速に行うことが望ましい。冷却速度が小さいと、加熱の場合と同様に凝結が進み過ぎる場合があり、所望の結晶子サイズを有するアナターズ型の二酸化チタンからなる固定化光触媒は得られない。冷却速度は、20℃/分以上とすることが好ましい。なお、急速に冷却する方法としては、空冷、水冷等の方法が利用できる。

【0033】前記の(1)の発明は、(2)の発明と同じく上記(1)の固定化光触媒の製造方法で、 $Zr/Ti$ （モル比）が0.3未満となるように二酸化ジルコニウムおよびジルコニウム塩のいずれか一方または両方が添加されたチタニアゾルを基材に塗布した後、300〜1000℃で焼成処理を施す方法である。

【0034】チタニアゾルに添加された二酸化ジルコニウムは、二酸化チタンの結晶の内部（結晶粒内）あるいは結晶粒界に分散して存在し、それによる一極のピン留め効果によって、二酸化チタンの焼成時におけるアナターズ晶の粒成長が抑えられる。また、二酸化ジルコニウムの添加は、800℃以上の高温焼成時に起こるアナタ

ースから光触媒活性の低いルチルへの転移の抑制にも有効である。なお、ジルコニウム塩も、焼成時に容易に酸化物になるので、二酸化ジルコニウムが添加された場合と同様の作用効果を有している。

【0035】したがって、これら二酸化ジルコニウムおよび/またはジルコニウム塩を添加することによって、前記(2)の発明で規定する焼成温度、あるいは焼成時間から若干外れる場合でも、結晶子サイズの小さい二酸化チタンからなる固定化光触媒を製造することが可能となる。つまり、焼成条件を緩和することができ、本発明の固定化光触媒を一層容易に製造することができる。

【0036】二酸化ジルコニウムは、超微粒の二酸化ジルコニウム（5〜10 nm）を水に懸濁させたり、ジルコニウムテトラ- $n$ -プロポキシド、ジルコニウムテトラ- $n$ -ブトキシド等のジルコニウムテトラアルコキシドや、四塩化ジルコニウム等を加水分解することによってジルコニアゾルとして調製することができる。また、ジルコニウム塩としては、オキシ塩化ジルコニウム、硝酸ジルコニウム等が利用できる。

【0037】塗布に用いる二酸化ジルコニウムおよび/またはジルコニウム塩を添加したチタニアゾルの調製は、別途調製したチタニアゾルに上記のジルコニアゾルあるいはジルコニウム塩を添加してもよいが、チタニアゾルを調製する際、チタニテトラアルコキシド等にジルコニウムテトラアルコキシドあるいはジルコニウム塩をあらかじめ混合しておくことにより簡便に行うことができる。

【0038】チタニアゾルに添加する二酸化ジルコニウムおよび/またはジルコニウム塩の量は $Zr/Ti$ （モル比）で0.3未満（ただし、0は含まない）である。 $Zr/Ti$ （モル比）が0.3（すなわち、 $Ti$ に對する $Zr$ の量が30 mol%）以上になると、焼成によってチタンとジルコニウムの混合酸化物、例えば $ZrTiO_4$ 等の生成が優先して起こるため、光触媒活性は著しく低下する。好ましくは1〜18 mol%、さらに好ましくは12〜18 mol%である。

【0039】焼成温度は300〜1000℃とする。焼成温度がその温度域の下限より低いと非晶質となり、上限を超えるるとルチル晶となるため、いずれの場合も光触媒活性の高い固定化光触媒は得られない。

【0040】焼成温度までの加熱は、二酸化ジルコニウムが二酸化チタンの焼成時におけるアナターズ晶の粒成長を効果的に抑制しているため、前記(2)の製造方法での加熱条件よりもかなり緩和な条件で行ってもよい。その条件に特に限定はないが、好ましい加熱速度は、3℃/分以下である。

【0041】焼成温度に達した後の保持時間（焼成時間）についても特に限定はない。しかし、過度に長時間にわたると生産効率が低下し、コストアップの原因とな

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るで、2時間以内とするのが好ましい。

【0042】 凝成後の冷却についても、加熱と同様、

(2)の方法に比べて緩和な条件で行ってもよいが、好ましい条件は、3℃/分以上である。

【0043】 上記(2)および(3)の方法によれば、本発明の固定化光触媒を特異的な手段を必要とせずに、比較的簡単に製造することができる。

【0044】 前記(4)の発明は、(1)の発明の固定化光触媒を用いて、特に有害物質を分解・除去する方法で、これらの固定化光触媒と有害物質とが接触した条件下で前記光触媒にバンドギャップ以上のエネルギーの光を照射する方法である。つまり、有害物質が固定化光触媒の触媒作用を受け得る状態の下で前記光触媒を構成する結晶内の充満層にある相当数の電子が静止層を越えて空層(伝導層)へ移るに足るエネルギーの光を照射するのである。

【0045】 ここでいう「有害物質」とは、人体に悪影響を及ぼす物質、あるいはその可能性がある物質のことであり、具体的には、NO<sub>x</sub>、SO<sub>x</sub>、フロン、アンモニア、硫化水素等の排ガスあるいは大気中に含まれる物質、アルヒド類、アミン類、メルカプタン類、アルコール類、BTX(ベンゼン、トルエン、キシレン)、フェノール類等の有機化合物、さらには、トリハロメタン、トリクロロエチレン等の有機ハロゲン化合物、除草剤、殺菌剤、殺虫剤等の種々の農薬、漂白剤やアミン類をはじめ種々の生化学的酵素要求量(BOD)の高い物質、界面活性剤、シアン化合物や硫黄化合物等の無機化合物、種々の重金属イオン等、さらには、細菌、放線菌、菌類、藻類などの微生物等、主として排水中に含まれるもの等が挙げられる。

【0046】 さらに、上記「有害物質」には、光触媒あるいはそれを用いた多機能部材の表面に直接付着する「付着物質」も含まれる。例えば、大腸菌、ブドウ球菌、緑膿菌、カビ等の菌類の胞、油、タバコのヤニ、指紋、雨垂れ、墨などである。

【0047】 また、前記の「固定化光触媒と有害物質とが接触した条件下」とは、固定化光触媒に上記の有害物質が直接付着している場合に於いて、例えば上記の有害物質が含まれる空気の他のガスや、水その他の媒体中に固定化光触媒が埋められ、有害物質が光触媒の触媒作用を受け得る状態の下にある場合をいう。

【0048】 このような条件下で(1)の発明の固定化光触媒にバンドギャップ以上のエネルギーの光を照射すると、光触媒作用が現現して、有害物質が効果的に分解・除去される。

【0049】 バンドギャップ以上のエネルギーの光としては、紫外線を含む光が好ましく、具体的には、太陽光や、蛍光灯、ブラックライト、水銀灯、キセノン灯等からの光があり、これらを光源として用いることができる。特に、波長が300-400nmの近紫外線を含む

光が好ましい。

【0050】 光の照射量や照射時間などは、分解・除去しようとする有害物質の量などによって適宜定めればよい。

【0051】

【実施例】

【実施例1】 チタンテトラ-*n*-ブトキシド40.5g(0.12mol)を純水エタノール75ml(ミリリットル)に加えた混合液を室温で30分間攪拌した後、水浴を用いて冷却した。その後、この混合液に、エタノール(75ml)、水(2.6ml)、硝酸(2ml)の混合液をゆっくりと滴下し、1時間攪拌した後、水浴から取り出して室温まで戻し、12時間攪拌を続けて透明なチタニウム溶液を得た。

【0052】 さらに、この溶液をスピコンタを用い、回転数300rpm、保持時間1分として、鏡面研磨したステンレス鋼板(材 SUS304:4cm×4cm×厚さ1mm)上に塗布した。その後直ちに、この基料を、炉内温度をあらかじめ50℃に設定した電熱炉に入れ、3分間焼成した後取り出し、冷却中で冷却した。この溶液の塗布、焼成操作を4回繰り返すことによって、ステンレス鋼表面に二酸化チタンを薄層状に形成させた固定化光触媒を作製した。

【0053】 なお、この光触媒の二酸化チタンは、X線回折によって調べた結果、図1に示すようにアナタース晶のパターンのみが認められた。また、Scherrerの式から求めた結晶子サイズ( $d_{111}$ )は1.5nmであり、透過型電子顕微鏡で観察した結晶粒径(約1.5nm)とはほぼ同じ値であった。表1に焼成温度、焼成時間および結晶子サイズを示す。

【0054】 この二酸化チタン固定化光触媒を試料として酢酸の分解実験を行った。

【0055】 まず、石英反応セル(内容量100cc)に、試料と濃度6.6mM(ミリモル)の酢酸水溶液70ml(酢酸含有量4.62mmol)を入れ、酸量を20分間透過した。次いで、25℃で逆置攪拌しながら、250Wの超音波水銀灯から、UVフィルター(東芝製UV-31)を通して4時間光照射を行った。その後、水溶液に含まれる酢酸の量をイオンクロマトグラフィーにより分析した結果、酢酸の分解による減少量は8.6μmolであった(図表に示す)。

【0056】 【実施例2】 チタンテトラ-*n*-ブトキシド80g(0.5mol)のイソプロパノールに加えた混合液を激しく攪拌している蒸留水500mlに滴下し、その後、硝酸(60%、以下、硝酸と60%硝酸をいう)5gを加えた。次いで、80℃で24時間攪拌し、真空下で濃縮し、二酸化チタンを15重量%含むチタニウム溶液を得、さらに2倍量のエタノールを加えることによって濃縮用溶液とした。

【0057】 この溶液を【実施例1】の場合と同様にスチ

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ンレス製試基材(SUS304:4cm×4cm×厚さ1mm)上に塗布した後、空気中で30分乾燥し、炉内温度が250℃の高温炉に入れ、30分間焼成した後取り出し、空気中で冷却した。このゾル液の塗布、焼成操作を4回繰り返すことによって、二酸化チタン固定化光触媒を作製した。

【0058】なお、この光触媒の二酸化チタンは、X線回折によって調べた結果、アナタース型であり、その結晶サイズ( $d_{111}$ )はおおよそ6.0nmであった。表1に焼成温度、焼成時間および結晶サイズを示す。

【0059】この二酸化チタン固定化光触媒を試料として、実施例1におけると同様の方法で酢酸の分解実験を行った。結果を表1に示したが、酢酸の分解による減少量は54.5μmolであった。

【0060】(実施例3~10) 焼成条件(焼成温度および焼成時間)を表1に示す条件とした以外はすべて実施例1と同様の方法で二酸化チタン固定化光触媒を得、同じく実施例1におけると同様の方法で酢酸の分解実験を行った。結果を表1に示すとおりであった。

【0061】(比較例1) 焼成時間を60分とした以外は実施例1と同様の方法で二酸化チタン固定化光触媒を作製した。この光触媒の二酸化チタンは、X線回折の結果、図1に示すようにアナタース晶のピークのみ認められたが、Scherrerの式から求めた結晶サイズ( $d_{111}$ )は32.5nm(透過型電子顕微鏡による観察では、33.6nm)で、本発明で規定する範囲から外れるものであった。

【0062】この二酸化チタン固定化光触媒を試料として、実施例1におけると同様の方法で酢酸の分解実験を行った。その結果は、表1に示したように、酢酸の分解による減少量は9.3μmolで、上記の実施例1に比べて著しく低かった。

【0063】(比較例2) 焼成温度を850℃とした以外は実施例1と同様の方法で二酸化チタン固定化光触媒を得た。この光触媒は、X線回折の結果、結晶サイズが35.5nmのアナタース晶と70~80nmの結晶粒を有するルチウム晶が共存した状態であった。

【0064】この二酸化チタン固定化光触媒を試料として、実施例1におけると同様の方法で酢酸の分解実験を行った。その結果、表1に示したように、酢酸の分解量はりであった。

【0065】(実施例11) チタンテトラ-*n*-ブトキシジド40.5g(0.12mol)とジルコニウムテトラ-*n*-ブトキシドを含む(濃度70%)する2-プロパノール溶液0.561g(1.2×10<sup>-3</sup>mol)を水素エタノール75mlに加えた混合液を容器で30分間攪拌した後、水浴を用いて冷却した。その後、この混合液に、エタノール(75ml) 水(2.6ml) 1. 調剤(2ml)の混合液をゆっくりと滴下し、1時間攪拌した後、水浴から取り出して室温で乾し、1

2時間攪拌を続けてチタニアゾルとジルコニアゾルの混合ゾル液(2 $r/n$ 1=1mol%)を得た。

【0066】さらに、このゾル液を、実施例1におけると同様の方法で、ステンレス製試基材(SUS304:4cm×4cm×厚さ1mm)上に塗布し、空気中50℃で60分間焼成した。このゾル液の塗布、焼成操作を4回繰り返すことによって、ステンレス鋼を被覆とする固定化光触媒を作製した。

【0067】図2に、この基材表面に形成された光触媒(二酸化ジルコニウムを含有する二酸化チタン)のX線回折図を示す。図示するように、二酸化チタンはアナタース型であった。一方、二酸化ジルコニウムに基づく回折パターンは認められなかった。また、Scherrerの式から求めた二酸化チタンアナタース晶の結晶サイズ( $d_{111}$ )は20.1nmであった。この結晶サイズは、同じ焼成条件で調製した調剤の比較例1の試料の結晶サイズ(32.5nm)と比べて明らかに小さく、二酸化ジルコニウムの添加によって二酸化チタンの結晶が抑制され、結晶粒の粗大化が防止されたことがわかる。

【0068】この固定化光触媒を試料として、実施例1におけると同様の方法で酢酸の分解実験を行った。結果は表1に示すとおりであった。

【0069】(実施例12) チタンテトラ-*n*-ブトキシド80gを50mlのイソプロパノールに加えた混合液を激しく攪拌している蒸留水500mlに滴下し、その後、調剤(60%)5gを加えた。次いで、60℃で24時間攪拌し、真空中で濃縮し、二酸化チタンを15重量%含むチタニアゾル液を得た。そのゾル液に、オキ塩化ジルコニウムを2.73g加えて(2 $r/n$ 1=3mol%)、十分攪拌した後、さらに2倍量のエタノールを加えることによって塗布用ゾル液を得た。

【0070】このゾル液を実施例1の場合と同様にステンレス製試基材(SUS304:4cm×4cm×厚さ1mm)上に塗布し、空気中50℃で60分間焼成した。このゾル液の塗布、焼成操作を4回繰り返すことによって、固定化光触媒を作製した。この基材上の光触媒はアナタース晶からなるものであり、その結晶サイズ( $d_{111}$ )は19.5nmであった。

【0071】この固定化光触媒を試料として、実施例1におけると同様の方法で酢酸の分解実験を行った。結果は表1に示すとおりであった。

【0072】(実施例13~17) ジルコニウムテトラ-*n*-ブトキシドを含む(濃度70%)する2-プロパノール溶液の量を1.69g、3.37g、6.73g、10.1g、13.48gおよび13.48gとした以外はすべて実施例11と同様の方法でステンレス鋼を被覆とする固定化光触媒を作製した。この基材表面に形成された光触媒(二酸化ジルコニウムを含有する二酸化チタン)は、X線回折の結果、図2に示すようにアナ



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ターズ晶のピークのみが認められ、二酸化ジルコニウムに基づく回折ピークは認められなかった。

【0073】これらの固定化光触媒を原料として、実施例1における同様の方法で酢酸の分解実験を行った。結果は表1に示すとおりで、酢酸の分解量は、次に示す比較例3（二酸化ジルコニウムが本発明で規定する量を超える固定化光触媒）に比べ大幅に上回った。

【0074】（比較例3）ジルコニウムテトラ-*n*-ブロボキシドを含有（濃度70%）する2-プロパノール溶液の量を16.84gとした以外はすべて実施例1と同様の方法でステンレス鋼を基材とする固定化光触媒を作製した。この基材表面に形成された光触媒（二酸化ジルコニウムを含有する二酸化チタン）は、X線回折の結果、図2に示すようにアナタース晶に基づく回折パターンは全く認められなかった。

【0075】この固定化光触媒を試料として、実施例1における同様の方法で酢酸の分解実験を行った。結果、

\*は表1に示すとおりで、酢酸はほとんど分解されなかった。これは、X線回折では検出されなかったが、チタンとジルコニウムの複合酸化物（ $ZrTiO_4$ 、等）が主に生成し、光触媒活性が著しく減少したことによるものである。

【0076】（実施例18）実施例16で調製したゾル液（ $Ti/Zr=18mol\%$ ）を用い、焼成温度を900℃、焼成時間を3分間とした以外はすべて実施例1と同様の方法でステンレス鋼を基材とする固定化光触媒を作製した。この基材表面に形成された光触媒は、結晶サイズ25.5nmのアナタース晶からなっており、ルチル晶は含まれていなかった。

【0077】この固定化光触媒を試料として、実施例1における同様の方法で酢酸の分解実験を行った。結果は表1に示すとおりであった。

【0078】

【表1】

表 1

No.	焼成温度 (℃)	焼成時間 (分)	Ti/Zr (mol%)	TiO <sub>2</sub> 結晶サイズ (nm)	酢酸分解量 (μmol)	
実 例	1	550	3	—	15.5	80.0
	2	250	30	—	6.0	64.5
	3	550	6	—	18.8	58.3
	4	650	16	—	19.0	52.7
	5	660	20	—	20.2	18.2
	6	650	30	—	24.1	6.2
	7	400	30	—	15.0	82.1
	8	900	30	—	27.3	1.6
比 較 例	9	500	3	—	18.3	93.1
	10	300	3	—	28.0	12.0
	11	550	60	1	20.1	17.7
	12	500	60	3	20.0	45.0
	13	550	60	3	19.5	35.6
	14	550	60	6	24.0	42.9
	15	550	60	12	22.5	49.5
	16	550	60	18	29.0	61.3
	17	550	60	24	23.5	56.2
	18	900	3	18	25.6	47.6
比 較 例	19	650	60	—	32.5	0.3
	20	850	3	—	35.5	0
	21	550	60	30	30.0	0.5

(注) \*は：本発明で規定する範囲から外れることを示す。

【0079】（実施例19）固定化光触媒の防汚効果を確かめるため、アセトアルデヒドを蒸気成分と想定してその分解実験を行った。

【0080】石英製反応セル（内容積10cc）に実施例16で作成した固定化光触媒を入れ、密閉容器ライン（合計内容積35cm<sup>3</sup>）に接続した。空気で置換し

たアセトアルデヒド（5000ppm）を系内を導入し、循環させながら250W超高压水銀灯から、紫外フィルター、UVフィルター（東京製UV-31）を通し、光照射を行った（紫外線強度15mW/cm<sup>2</sup>）。なお、アセトアルデヒドの分解による減少量はラインに接続されているガスクロマトグラフを用いて測定した。

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【0081】その結果、図3に示すように、アセトアルデヒドは経時的に減少し、120分後には、検出不能なレベル(10ppm以下)になった。

【0082】(比較例2)比較例1で作製した固定化光触媒を用いて、実施例19におけると同様の方法でアセトアルデヒドの分解実験を行った。

【0083】結果は図3に示すように、120分後のアセトアルデヒドの残存濃度は約3500ppmで、実施例19に比べアセトアルデヒドの分解量ははるかに少なかった。

【0084】(実施例20)固定化光触媒の抗菌効果を確認するため、大腸菌(Escherichia coli W3110株)に対する殺菌効果を調査した。

【0085】実施例1で作製した固定化光触媒を試料として用い、その表面をあらかじめ70%エタノールで殺菌した後、大腸菌を $2.5 \times 10^5$ 個/ml含む生理食塩水0.2ml(大腸菌数: $5 \times 10^4$ 個)を、0.025mlずつ8箇所に分けてその表面に滴下した。次に、相対湿度95%の条件下で、250W超高温圧水銀灯を用い、上部から、減光フィルター、UVフィルター(東芝製UV-35)を通して15分間光照射を行った(紫外線強度1mW/cm<sup>2</sup>)。

【0086】その後、試料の上の菌数を生理食塩水9.8mlで洗い流し、それを標準寒天培地に希釈塗布し、35℃で48時間培養した後、生育したコロニーを計数することによって菌数を測定した。抗菌性の評価は、同じ条件で、大腸菌を含む生理食塩水を、二酸化チタンを形成(コーティング)していない普片(SUS304)表面に滴下して15分間光照射したものと、実施例1で作製した固定化光触媒の表面に滴下して15分間暗所に保持したものとについて、上記と同様に測定した菌数(それぞれ $4.8 \times 10^3$ 個および $4.7 \times 10^3$ 個)を基準として行った。

【0087】その結果、光照射することによって生育大腸菌数は $1.6 \times 10^3$ 個となり、優れた抗菌性が認められた。

【0088】(実施例21)基材として石英板(4cm×4cm×厚さ1mm)を用いた以外はすべて実施例1と同様の方法で石英板表面に二酸化チタンを薄層状に形成させた固定化光触媒を作製した。この光触媒の結晶構造をX線回折によって調べた結果、二酸化チタンはアナタース晶からなるものであり、その結晶サイズは14.5nmであった。

【0089】この二酸化チタン固定化光触媒を試料として用い、テトラクロロエチレンの分解実験を行った。なお、テトラクロロエチレンは、洗剤、殺菌剤、樹脂等の溶剤として利用されており、地下水の汚染要因の一つとして問題視されている物質である。

【0090】まず、石英反応セル(内容積100cc)に30ppmの濃度のテトラクロロエチレンの水溶

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液40mlを入れ、その中に試料を浸し、液温を20分間バブリングした後、250W超高温圧水銀灯から、UVフィルター(東芝製UV-29)を通して4時間光照射を行った。その後、水浴槽に含まれるテトラクロロエチレンの量をガスクロマトグラフを用いて測定した。その結果、テトラクロロエチレンの濃度は3.2ppmに減少していた。

【0091】(実施例22)基材として樹脂製の鏡像銅板(5cm×5cm×厚さ1mm)を用い、焼成時間を2分とした以外はすべて実施例2と同様の方法で鏡像銅板表面に二酸化チタンを薄層状に形成させた固定化光触媒を作製した。この光触媒の結晶構造をX線回折によって調べた結果、二酸化チタンはアナタース晶からなるものであり、その結晶サイズは5.8nmであった。

【0092】この光触媒を試料として用い、以下の要領で試料表面に付着させたタバコのヤニの除去試験を行った。

【0093】試料表面にタバコ1本のヤニを強制的に付着させた後、250W超高温圧水銀灯から、減光フィルター、UVフィルター(東芝製UV-35)を通して光照射(紫外線強度5mW/cm<sup>2</sup>)を行いながら色計を用いて黄色の目玉となるb値の変化を測定することにより、ヤニの減少を評価した。

【0094】その結果、b値は、光照射前の1.6、5から、2時間の光照射ではほぼ1となり、見た目にも普片として用いた塗膜の色(白色)が戻ったことから、ヤニが効果的に除去されていることが確認された。一方、上記のような処理を行っていない塗膜銅板を用い、同様の試験を行ったところ、b値は、光照射前の1.3、4から、2時間の光照射では8.2にしかならず、ヤニは試料表面上にかなり残っていた。

【0095】

【発明の効果】本発明の固定化光触媒は反応活性が高く、大気中あるいは水中の有害物質、汚れた付着物の分解、除去に対して優れた効果を示す。したがって、基材として金属、ガラス、セラミックス等を用いれば、抗菌、防臭、防泥、防かび、環境汚染物質の分解等の作用効果が付与された内装材、建材等の部材を容易に提供することができる。特に、本発明の有害物質の分解、除去方法によれば、種々の付着物質も含め、人体に悪影響を及ぼすからしくはその可能性がある有害物質を効果的に分解・除去することができる。

【0096】この光触媒は、本発明の製造方法によれば、比較的安価な原料を用い、特別な設備および操作を必要とせず、また、焼成時間が短く、従来、従来の固定化光触媒に比べて低コストで製造することが可能である。

【図面の簡単な説明】

【図1】実施例1および比較例1で用いた試料についてのX線回折図である。

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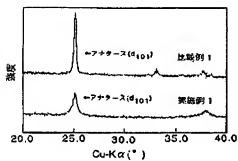
15

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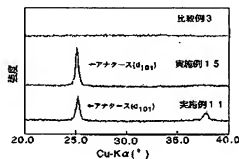
【図2】実施例11、15および比較例3で用いた試料についてのX線回折図である。

\* 【図3】実施例19および比較例4の実験結果で、アセトアルデヒドの分解の経時変化を示す図である。

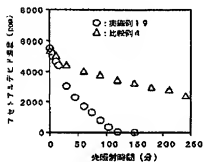
【図1】



【図2】



【図3】



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(54) FIXED PHOTOCATALYST, PREPARATION THEREOF, AND METHOD FOR DECOMPOSITION-REMOVING HARMFUL SUBSTANCE

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## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a fixed photocatalyst which has high photocatalytic reaction efficiency and indicates good effects for the decomposition, etc., of dirt (sticking dirty substances) on the surface of solids and harmful substances in the air or drainage, a method for preparing the catalyst, and a method for decomposition-removing harmful substances using the catalyst.

SOLUTION: In a fixed photocatalyst, a thin film of anatase-type titanium dioxide of 5-30nm average crystal size is fixed on the surface of a base material. Harmful substances in contact with the catalyst are decomposition-removed effectively by being irradiated with high energy light. The catalyst can be prepared by a method in which titania sol applied on the base material is heated at a prescribed temperature (250-800°C) and burned for a short time (within 30min). The use of titania sol added with a prescribed quantity of zirconium dioxide and/or zirconium salt can alleviate the burning conditions.

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LEGAL STATUS

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**CLAIMS**

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[Claim(s)]

[Claim 1] The photocatalyst characterized by fixing to a base material front face the anatase titanium dioxide whose average microcrystal size is 5-30nm in the shape of a thin film.

[Claim 2] The manufacture approach of the fixed photocatalyst according to claim 1 characterized by performing baking processing which heats to 250-800 degrees C, and is held less than 30 minutes at the temperature after applying a titania sol to a base material.

[Claim 3] The manufacture approach of the fixed photocatalyst according to claim 1 characterized by performing baking processing at 300-1000 degrees C after applying to a base material the titania sol by which both the zirconium dioxide, and zirconium both [ either or ] were added so that Zr/Ti (mole ratio) may become less than 0.3.

[Claim 4] The decomposition / clearance approach of the harmful matter characterized by irradiating the light of the energy more than a band gap at said fixed photocatalyst under the conditions which a fixed photocatalyst according to claim 1 and harmful matter contacted.

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[Translation done.]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention has effectiveness in deodorization, antifouling (dirt prevention on the front face of a solid-state), sterilization, etc., has the operation which disassembles and removes harmful matter, such as an atmospheric pollutant or a pollutant under wastewater, and relates to the fixed photocatalyst which can apply photoelectricity chemistry, organic synthesis, etc. further, its manufacture approach, and the decomposition / clearance approach of the harmful matter using the photocatalyst.

[0002]

[Description of the Prior Art] If light is irradiated at a semi-conductor, the electron which has a reduction operation strong against the exposure side, and the electron hole which has the strong oxidation will be generated, and the molecule in contact with a semi-conductor will be disassembled by the oxidation reduction operation.

[0003] such an operation of recent years and a semi-conductor, i.e., a photocatalyst operation, -- NOx etc. -- the attempt applied to various environmental clarification techniques, such as disassembly of an atmospheric pollutant, deodorization, antifouling, sterilization, and water purification, is performed energetically. However, there are very few examples put in practical use by the effectiveness of a photocatalysis being low in the actual condition.

[0004] From the former, a semi-conductor photocatalyst is powdered and has been used in the condition made to suspend in a solution, or the condition of having fixed in the shape of a thin film on the base material. From a viewpoint of maintaining the activity of a photocatalyst highly, although an activity, in the large suspension condition of surface area is desirable, an activity in the condition which handling is easy and has broad application from a practical use side of having fixed can say that it is far promising.

[0005] Therefore, the titanium-dioxide fixed photocatalyst which the various approaches of raising the activity of the photocatalyst (this is hereafter called "fixed photocatalyst") which fixed to the base material the semi-conductor which has a photocatalyst operation are proposed, for example, becomes JP,7-100378,A from the crystal of an anatase is indicated. This photocatalyst adds an alcoholic amine to the sol of the titanium dioxide used for spreading of a up to [ a base material ], and is manufactured by carrying out heating temperature up slowly to the burning temperature of 600-700 degrees C. However, since photocatalyst activity sufficient in this fixed photocatalyst is not acquired and an alcoholic amine cannot disperse easily, there is also a problem of requiring a lot of energy at the time of manufacture.

[0006] Moreover, the manufacture approach of the fixed photocatalyst to which crystal growth of the particle of the titanium dioxide contained in it is carried out is indicated by JP,6-293519,A by carrying out hydrothermal processing of the titania sol used for spreading beforehand. Although this photocatalyst has comparatively high catalytic activity, the titania sol which carried out crystal growth is hard to be applied at homogeneity to a base material, and has the problem of being easy to exfoliate after baking. Furthermore, in order that solution concentration, temperature, a pressure, etc. may take delicate control to hydrothermal processing while it is a reaction under an elevated temperature and high voltage, it is not suitable for the mass production of a photocatalyst.

[0007]

[Problem(s) to be Solved by the Invention] This invention is under the situation that it mentioned above, and its photocatalysis effectiveness is high. Therefore, the harmful matter contained in wastewater among deodorization, antifouling, antibacterial, and atmospheric air etc. The effectiveness which was excellent to (for example, disassembly of NOx, agricultural chemicals, an organic halogenated compound, etc.), defanging, etc. is shown. And it makes offering a suitable fixed photocatalyst and its suitable manufacture

approach, and the decomposition / clearance approach of the harmful matter using the photocatalyst also from fields, such as profitability, stability, and safety, as a technical problem.

[0008]

[Means for Solving the Problem] As a result of repeating examination that this invention person should develop the fixed photocatalyst which used the titanium dioxide and in which high reaction effectiveness is shown, after applying a titania sol to a base material, by calcinating and carrying out crystal growth It can consider as the anatase titanium dioxide whose average microcrystal size is 5-30nm. When the specific surface area of the fixed titanium dioxide increased, and labile sites, such as a coordination partial saturation point and a lattice defect, increased and the enhancement effect of the oxidation reduction force was also further added at the time of a quantum size effect manifestation, it found out that photocatalyst activity improved remarkably.

[0009] Moreover, the fixed photocatalyst which has such a property carried out the knowledge of manufacturing still more easily being possible by being able to manufacture by making baking after applying a titania sol to a base material front face into a short time, and adding the salt of the zirconium dioxide of the specified quantity, or a zirconium to the titania sol used for spreading further.

[0010] This invention was made based on these knowledge, and the summary is in the fixed photocatalyst of following (1), (2), its manufacture approach of (3), and the decomposition / clearance approach of harmful matter of using the fixed photocatalyst of (4).

[0011] (1) The photocatalyst characterized by fixing to a base material front face the anatase titanium dioxide whose average microcrystal size is 5-30nm in the shape of a thin film.

[0012] (2) The manufacture approach of a fixed photocatalyst given in the above (1) characterized by performing baking processing which heats to 250-800 degrees C, and is held less than 30 minutes at the temperature after applying a titania sol to a base material.

[0013] (3) The manufacture approach of a fixed photocatalyst given in the above (1) characterized by performing baking processing at 300-1000 degrees C after applying to a base material the titania sol by which both the zirconium dioxide, and zirconium both [ either or ] were added so that Zr/Ti (mole ratio) may become less than 0.3.

[0014] (4) The decomposition / clearance approach of the harmful matter characterized by irradiating the light of the energy more than a band gap at said fixed photocatalyst under the conditions to which the fixed photocatalyst and harmful matter of a publication contacted the above (1).

[0015] Although the aforementioned "average microcrystal size" means the diameter of crystal grain which carried out direct observation with the transmission electron microscope fundamentally, since this value is well in agreement with the microcrystal size computed using the formula of Scherrer from the peak of ANATASU (d101) by the X diffraction, by this invention, which these values may be used for it as average microcrystal size. In addition, there is no semantics (definition) special to "an average", and even if there is a less than 5nm thing or a thing exceeding 30nm a little, the arithmetic mean of two or more microcrystal sizes should just be in within the limits which is 5-30nm.

[0016]

[Embodiment of the Invention] Hereafter, this invention (above (1) invention of - (4)) is explained to a detail.

[0017] Invention of the above (1) is a fixed photocatalyst (this is called "fixed photocatalyst of this invention") characterized by being obtained as a result of carrying out crystal growth of the thin film-like titanium dioxide by baking, and the microcrystal size being within the limits of 5-30nm on an average, after applying a titania sol to a base material front face.

[0018] In the fixed photocatalyst of this invention, the crystal structure of a titanium dioxide must be an anatase first. It is because a photocatalyst with high photocatalyst activity will not be obtained if it is not an anatase as the example mentioned later shows.

[0019] Furthermore, it is required to be in within the limits the average microcrystal size (only henceforth "microcrystal size") of whose is 5-30nm. Microcrystal size's being less than 5nm is that the mean particle diameter of the titanium dioxide contained in a titania sol is about 5nm, and it is substantially difficult to manufacture the titanium dioxide of such a particle. On the other hand, if microcrystal size exceeds 30nm, photocatalyst activity will fall remarkably.

[0020] Far-reaching ingredients, such as an ingredient of the arbitration chosen from organic materials, such as inorganic materials, such as various kinds of metallic materials, such as a steel plate which galvanized stainless steel, carbon steel, zinc, etc. or an aluminum plate, and a titanium plate, and ceramics, pottery, glass, resin, timber, and activated carbon, as a base material which fixes a titanium dioxide, or composite

material which consists of two or more sorts of them, can be used. The member to which paint has already been performed can also be used. Moreover, there may be no definition in any way also about the configuration of a base material, and you may be tabular [ of a thick plate, sheet metal, etc. ], a globular shape like a bead, or the complicated configuration offered as a product as it is. Moreover, porosity or the substantial compacta is sufficient as a front face.

[0021] There is especially no definition about the thickness of a titanium dioxide. There is an inclination which shows such high photocatalyst activity that it generally becomes thick. However, since the improvement effectiveness of photocatalyst activity will not be accepted but exfoliation of the film etc. will become easy to take place if thickness exceeds 2 micrometers, it is desirable that it is 2 micrometers or less.

[0022] By the light from sunlight, a fluorescent lamp, the black light, a mercury-vapor lamp, a xenon LGT, etc., this fixed photocatalyst discovers a photocatalyst operation and shows the effectiveness which was excellent to disassemble of the harmful matter contained in wastewater among antibacterial, deodorization, antifouling, and atmospheric air etc., defanging, etc. Moreover, this fixed photocatalyst is excellent in stability, safety (there is no toxicity), etc., can be suitably used as inner package material, building materials, glass, a panel, a tile, etc., is faced using it, and does not need energy at all (energy saving), but it also has the advantage of being maintenance free.

[0023] Invention of the above (2) is the manufacture approach of the fixed photocatalyst the above (1), and after it applies a titania sol to a base material, it is the approach of performing baking processing which heats to 250-800 degrees C (burning temperature), and carries out short-time (less than 30 minutes) maintenance at the temperature.

[0024] Preparation of a titania sol can be performed by making water suspend the titanium dioxide (5-10nm) of a super-particle, or hydrolyzing titanium tetra-alkoxides, such as a titanium tetra-methoxide, titanium tetra-ethoxide, titanium tetra-n-propoxide, titanium tetra-i-propoxide, and titanium tetra-n-butoxide, titanium acetylacetonate, a titanium tetrachloride, etc. Moreover, to a sol, alcoholic amines, such as diethanolamine and triethanolamine, and desiccation inhibitors, such as 1,3-propanediol, may be added.

[0025] Thus, the mean particle diameter of the titanium dioxide contained in the obtained titania sol is about 5-10nm, and let it be the titanium-dioxide fixed photocatalyst of desired microcrystal size (5-30nm) by making a base material front face apply, calcinate and carry out crystal growth of this.

[0026] Spin coating, DIP coating, spray coating, bar coating, etc. can perform spreading of the titania sol to a base material.

[0027] Although a fixed photocatalyst is obtained by calcinating after applying a titania sol to a base material, since sintering of metallic oxides, such as a titanium dioxide fixed in the shape of a thin film on the base material front face, takes place very promptly and crystal grain becomes large, on the usual baking conditions, the fixed photocatalyst of this invention with which the microcrystal size mentioned above consists of a titanium dioxide in the range which is 5-30nm is not obtained.

[0028] Then, baking is performed on condition that predetermined [ above ]. That is, after heating to burning temperature after applying a titania sol to a base material, and carrying out predetermined time maintenance at the temperature, baking processing to cool is performed. Baking is good in a line with the condition (room temperature condition) of having applied, or may be performed from the condition of having dried around after [ spreading ] 100 degrees C.

[0029] Let burning temperature be a 250-800-degree C temperature region. When burning temperature is lower than 250 degrees C, a titanium dioxide is still amorphous, on the other hand, if it exceeds 800 degrees C, crystal grain will grow and it will become large too much, or rutile \*\* appears, and the fixed photocatalyst which has high photocatalyst activity is not obtained.

[0030] It is desirable to perform heating to burning temperature quickly. When heating is not performed quickly, by the time it reaches the aforementioned burning temperature, sintering of a titanium dioxide progresses too much, and crystal grain may make it big and rough. A desirable heating rate is above by 30-degree-C/. In addition, in order to heat quickly, the heat treating furnace is beforehand heated to predetermined temperature, and it is suitable to use the approach of inserting in directly the base material which applied the titania sol into it etc.

[0031] The holding time (firing time) after reaching burning temperature is made into less than 30 minutes. Since width of face is in burning temperature, when it is actually set as the lower temperature in the aforementioned temperature requirement as a burning temperature, firing time is lengthened, and when it is set as higher temperature, it adjusts shortening etc. suitably. In addition, it is desirable when making burning temperature into the range of 400-700 degrees C, and making firing time into less than 10 minutes obtains the fixed photocatalyst which has high photocatalyst activity.



[0032] Although after baking is cooled, it is desirable to also perform cooling quickly. If a cooling rate is small, the fixed photocatalyst which consists of a titanium dioxide of the anatase which sintering may progress too much like the case where it is heating, and has desired microcrystal size will not be obtained. 20-degree-C thing considered as the above by /of a cooling rate is desirable. In addition, approaches, such as air cooling and water cooling, can be used as an approach of cooling quickly.

[0033] The aforementioned invention of (3) is the manufacture approach of the fixed photocatalyst the above (1) as well as invention of (2), and after it applies to a base material the titania sol by which both the zirconium dioxide, and zirconium both [ either or ] were added so that Zr/Ti (mole ratio) may become less than 0.3, it is the approach of performing baking processing at 300-1000 degrees C.

[0034] The zirconium dioxide added by the titania sol distributes and exists in the interior (inside of crystal grain) or the grain boundary of a crystal of a titanium dioxide, and grain growth of ANATASU \*\* at the time of baking of a titanium dioxide is suppressed according to a kind of pin stop effectiveness by it. Moreover, addition of a zirconium dioxide is effective also in control of the transition to the rutile with low photocatalyst activity which happens at the time of elevated-temperature baking of 800 degrees C or more from ANATASU. In addition, since a zirconium salt also becomes oxide easily at the time of baking, it has the same operation effectiveness as the case where a zirconium dioxide is added.

[0035] Therefore, even when separating a little from the burning temperature specified by invention of the above (2) by adding these zirconium dioxides and/or a zirconium salt, or firing time, it becomes possible to manufacture the fixed photocatalyst which consists of a titanium dioxide with small microcrystal size. That is, baking conditions can be eased and the fixed photocatalyst of this invention can be manufactured still more easily.

[0036] A zirconium dioxide can be prepared as a zirconia sol by making water suspend the zirconium dioxide (5-10nm) of a super-particle, or hydrolyzing zirconium tetra-alkoxides, such as zirconium tetra-n-propoxide, zirconium tetra-i-propoxide, and zirconium tetra-n-butoxide, a zirconium tetrachloride, etc. Moreover, zirconium oxychloride, zirconium nitrate, etc. can be used as a zirconium salt.

[0037] Although an above-mentioned zirconia sol or an above-mentioned zirconium salt may be added to the titania sol prepared separately, preparation of the titania sol which added the zirconium dioxide and/or zirconium salt which are used for spreading can be performed simple by mixing the zirconium tetra-alkoxide or the zirconium salt beforehand to the titanium tetra-alkoxide etc., in case a titania sol is prepared.

[0038] The amount of the zirconium dioxide added to a titania sol and/or a zirconium salt is made less than into 0.3 (however, 0 does not contain) by Zr/Ti (mole ratio). if Zr/Ti (mole ratio) becomes more than 0.3 (that is, the amount of Zr to Ti 30-mol%) -- baking -- the multiple oxide 4 of titanium and a zirconium, for example, ZrTiO<sub>4</sub>, etc. -- in order that generation may have priority and start, photocatalyst activity falls remarkably. It is 12-18-mol% preferably [ it is desirable and ] to 1-18-mol % and a pan.

[0039] Burning temperature is made into 300-1000 degrees C. Since it will become amorphous if burning temperature is lower than the minimum of this temperature region, and it will become rutile \*\* if an upper limit is exceeded, as for the high fixed photocatalyst of photocatalyst activity, neither of the cases is acquired.

[0040] Since the zirconium dioxide has controlled effectively grain growth of ANATASU \*\* at the time of baking of a titanium dioxide, heating to burning temperature may be performed on conditions quite milder than the heating conditions in the manufacture approach of the above (2). Although there is especially no definition in the condition, a desirable heating rate is above by 3-degree-C/.

[0041] There is especially no definition also about the holding time (firing time) after reaching burning temperature. However, since productive efficiency will fall and it will become the factor of a cost rise if long duration is covered too much, considering as less than 2 hours is desirable.

[0042] Although you may carry out on mild conditions about cooling after baking as well as heating compared with the approach of (2), desirable conditions are above by 3-degree-C/.

[0043] According to the above (2) and the approach of (3), the fixed photocatalyst of this invention can be comparatively manufactured easily by low cost, without needing a special means.

[0044] Invention of the above (4) is the approach of using the fixed photocatalyst of invention of (1), and disassembling and removing especially harmful matter, and is the approach of irradiating the light of the energy more than a band gap at said photocatalyst under the conditions which such fixed photocatalysts and harmful matter contacted. That is, the light of the energy which is sufficient for the electron of the considerable number in the filled band in the crystal which constitutes said photocatalyst from under the condition that harmful matter can receive the catalysis of a fixed photocatalyst moving to an empty band (conduction band) over a forbidden band is irradiated.

[0045] "Harmful matter" here is the matter which has an adverse effect on the body, or matter with the possibility. Specifically The matter contained in exhaust gas, such as NO<sub>x</sub>, SO<sub>x</sub>, chlorofluorocarbon, ammonia, and a hydrogen sulfide, or atmospheric air, To organic compounds, such as aldehydes, amines, mercaptans, alcohols, BTX (benzene, toluene, xylene), and phenols, and a pan Organic halogenated compounds, such as trihalomethane and a trichloroethylene, a herbicide, Various agricultural chemicals, such as a germicide and an insecticide, protein, and amino acid are begun. The matter with various high biochemical oxygen demand (BOD), Things further contained [ microorganisms /, such as bacteria, an Actinomyces, a fungus, and algae, ] mainly during wastewater, such as inorganic compounds, such as a surfactant, a cyanide compound, and a sulfur compound, and various heavy metal ions, are mentioned. [0046] Furthermore, "the quality of an affix" which adheres to the front face of the multifunctional member which used a photocatalyst or it directly above "harmful matter" is contained. For example, they are an oil besides funguses, such as *Escherichia coli*, *Staphylococcus*, *Pseudomonas aeruginosa*, and mold, the tar of tobacco, a fingerprint, raindrops, mud, etc.

[0047] Moreover, a fixed photocatalyst is placed into the gas of air and others by which the above-mentioned harmful matter else [ when the above-mentioned harmful matter has adhered to the fixed photocatalyst directly ] is contained, and the liquid of water and others, and "the bottom of the condition which a fixed photocatalyst and harmful matter contacted" of the above says the case where it is under the condition that harmful matter can receive the catalysis of a photocatalyst.

[0048] If the light of the energy more than a band gap is irradiated under such conditions at the fixed photocatalyst of invention of (1), a photocatalyst operation will be discovered, and harmful matter will be disassembled and removed effectively.

[0049] As a light of the energy more than a band gap, light including ultraviolet rays is desirable, there is light from sunlight, a fluorescent lamp, the black light, a mercury-vapor lamp, a xenon LGT, etc., and, specifically, these can be used as the light source. The light which includes especially the near ultraviolet ray whose wavelength is 300-400nm is desirable.

[0050] What is necessary is just to define a dose, irradiation time, etc. of light suitably with the amount of the harmful matter which it is going to disassemble and remove etc.

[0051]

[Example]

(Example 1) After stirring the mixed liquor which added titanium tetra-*n*-butoxide 40.5g (0.12 mols) to dehydrolation ethanol 75ml (milliliter) for 30 minutes at a room temperature, it cooled using the ice bath. Then, after dropping slowly the mixed liquor of ethanol (75ml), water (2.6ml), and a nitric acid (2ml) and stirring it into this mixed liquor for 1 hour, transparent titania sol liquid was obtained for stirring continuously [ it took out from the ice bath, returned to the room temperature, and / for 12 hours ].

[0052] Furthermore, it applied on the base material made from stainless steel (1mm in SUS304:4cmx4cmx thickness) which carried out mirror polishing of this sol liquid as rotational frequency 300rpm and holding-time 1 minute using the spin coater. After that, promptly, this base material was cooled in ejection and air, after putting whenever [ furnace temperature ] into the electric heat furnace beforehand set as 550 degrees C and calcinating it for 3 minutes. The fixed photocatalyst which made the titanium dioxide form in a stainless steel front face in the shape of a thin film was produced by repeating spreading of this sol liquid, and baking actuation 4 times.

[0053] In addition, as a result of an X diffraction's investigating the titanium dioxide of this photocatalyst, as shown in drawing 1, only the pattern of ANATASU \*\* was accepted. Moreover, the microcrystal size (d101) for which it asked from the formula of Scherrer was 15.5nm, and was the almost same value as the diameter (about 15nm) of crystal grain observed with the transmission electron microscope. Burning temperature, firing time, and microcrystal size are shown in a table 1.

[0054] The decomposition experiment of an acetic acid was conducted by making this titanium-dioxide fixed photocatalyst into a sample.

[0055] First, a sample and 70ml (the acetic-acid content mol of 462micro) of acetic-acid water solutions of concentration 6.6mM (millimol) were put into the reaction cel made from a quartz (100 cc of inner capacity), and oxygen was \*\*\*\*\* (ed) in it for 20 minutes. Subsequently, the optical exposure was performed through the UV filter (Toshiba UV- 31) from the ultrahigh pressure mercury lamp of 250W for 4 hours, carrying out porcelain stirring at 25 degrees C. Then, as a result of ion chromatography's analyzing the amount of the acetic acid contained in a water solution, the decrement by disassembly of an acetic acid was 80micromol (it displays on this table).

[0056] (Example 2) It was dropped at 500ml of distilled water which has agitated violently the mixed liquor

which added titanium tetra-*i*-propoxide 80g to 50ml isopropanol, and 5g (a nitric acid means a nitric acid 60% hereafter 60%) of nitric acids was added after that. Subsequently, it agitated at 80 degrees C for 24 hours, and condensed under the vacuum, the titania sol liquid which contains a titanium dioxide 15% of the weight was obtained, and it considered as the sol liquid for spreading by adding the ethanol of the amount of 2 double to a pan.

[0057] After applying this sol liquid like the case of an example 1 on the base material made from stainless steel (1mm in SUS304:4cmx4cm thickness), it dried in air for 30 minutes, it put into the electric heat furnace whenever [ furnace temperature / whose ] is 250 degrees C, and after calcinating for 30 minutes, it cooled in ejection and air. The titanium-dioxide fixed photocatalyst was produced by repeating spreading of this sol liquid, and baking actuation 4 times.

[0058] In addition, the titanium dioxide of this photocatalyst was an anatase as a result of an X diffraction's investigating, and that microcrystal size (d101) was about 6.0nm. Burning temperature, firing time, and microcrystal size are shown in a table 1.

[0059] Also in the example 1, the decomposition experiment of an acetic acid was conducted by the same approach by making this titanium-dioxide fixed photocatalyst into a sample. Although the result was shown in a table 1, the decrement by disassembly of an acetic acid was 54.5micromol.

[0060] (Examples 3-10) Except [ all ] having considered as the conditions which show baking conditions (burning temperature and firing time) in a table 1, the titanium-dioxide fixed photocatalyst was obtained by the same approach as an example 1, and, similarly the decomposition experiment of an acetic acid was conducted by the same approach in the example 1. The result was as being shown in a table 1.

[0061] (Example 1 of a comparison) The titanium-dioxide fixed photocatalyst was produced by the same approach as an example 1 except having made firing time into 60 minutes. Although only the peak of ANATASU \*\* was accepted as the titanium dioxide of this photocatalyst was shown in drawing 1 as a result of an X diffraction, the microcrystal size (d101) for which it asked from the formula of Scherrer was 32.5nm (by observation by the transmission electron microscope, it is 33.0nm), and was that from which it separates from the range specified by this invention.

[0062] Also in the example 1, the decomposition experiment of an acetic acid was conducted by the same approach by making this titanium-dioxide fixed photocatalyst into a sample. As the result was shown in a table 1, the decrement by disassembly of an acetic acid was 0.3micromol, and was remarkably low compared with the above-mentioned example 1.

[0063] (Example 2 of a comparison) The titanium-dioxide fixed photocatalyst was obtained by the same approach as an example 1 except having made burning temperature into 850 degrees C. This photocatalyst suited the condition that ANATASU \*\* whose microcrystal size is 35.5nm, and rutile \*\* which has a 70-80nm diameter of crystal grain were intermingled, as a result of the X diffraction.

[0064] Also in the example 1, the decomposition experiment of an acetic acid was conducted by the same approach by making this titanium-dioxide fixed photocatalyst into a sample. Consequently, as shown in a table 1, the amount of decomposition of an acetic acid was 0.

[0065] (Example 11) After stirring the mixed liquor which added 0.561g (1.2x10 to 3 mol) of 2-propanol solutions containing (70% of concentration) titanium tetra-*n*-butoxide 40.5g (0.12 mols) and zirconium tetra-*n*-propoxide to dehydration ethanol 75ml for 30 minutes at a room temperature, it cooled using the ice bath. Then, after dropping slowly the mixed liquor of ethanol (75ml), water (2.6ml), and a nitric acid (2ml) and stirring it into this mixed liquor for 1 hour, the mixed sol liquid (Zr/Ti=one-mol%) of a titania sol and a zirconia sol was obtained for stirring continuously [ it took out from the ice bath, returned to the room temperature, and / for 12 hours ].

[0066] Furthermore, this sol liquid was applied by the same approach also in the example 1 on the base material made from stainless steel (1mm in SUS304:4cmx4cm thickness), and was calcinated for 60 minutes at 550 degrees C among air. The fixed photocatalyst which uses stainless steel as a base material was produced by repeating spreading of this sol liquid, and baking actuation 4 times.

[0067] X diffraction drawing of the photocatalyst (titanium dioxide containing a zirconium dioxide) formed in this base material front face at drawing 2 is shown. The titanium dioxide was an anatase so that it might illustrate. On the other hand, the diffraction pattern based on a zirconium dioxide was not accepted. Moreover, the microcrystal size (d101) of titanium-dioxide ANATASU \*\* for which it asked from the formula of Scherrer was 20.1nm. This microcrystal size is clearly small compared with the microcrystal size (32.5nm) of the sample of the aforementioned example 1 of a comparison prepared on the same baking conditions, and it turns out that sintering of a titanium dioxide was controlled by addition of a zirconium dioxide, and big and rough-ization of crystal grain was prevented.

[0068] Also in the example 1, the decomposition experiment of an acetic acid was conducted by the same approach by making this fixed photocatalyst into a sample. The result was as being shown in a table 1.

[0069] (Example 12) It was dropped at 500ml of distilled water which has agitated violently the mixed liquor which added titanium tetra-*i*-propoxide 80g to 50ml isopropanol, and 5g (60%) of nitric acids was added after that. Subsequently, it agitated at 80 degrees C for 24 hours, and condensed under the vacuum, and the titania sol liquid which contains a titanium dioxide 15% of the weight was obtained. After adding 2.73g of zirconium oxychlorides (Zr/Ti=three-mol%) and agitating them enough in the sol liquid, the sol liquid for spreading was obtained by adding the ethanol of the amount of 2 double to a pan.

[0070] This sol liquid was applied like the case of an example 1 on the base material made from stainless steel (1mm in SUS304:4cmx4cmx thickness), and was calcinated for 60 minutes at 500 degrees C among air. The fixed photocatalyst was produced by repeating spreading of this sol liquid, and baking actuation 4 times. The photocatalyst on this base material consists of ANATASU \*\*, and that microcrystal size (d101) was 19.5nm.

[0071] Also in the example 1, the decomposition experiment of an acetic acid was conducted by the same approach by making this fixed photocatalyst into a sample. The result was as being shown in a table 1.

[0072] (Examples 13-17) The fixed photocatalyst which uses stainless steel as a base material by the same approach as an example 11 was produced except [ all ] having set the amount of the 2-propanol solution containing (70% of concentration) zirconium tetra-*n*-propoxide to 1.69g, 3.37g, 6.73g, 10.1g, 13.48g, and 13.48g. As the photocatalyst (titanium dioxide containing a zirconium dioxide) formed in this base material front face was shown in drawing 2 as a result of an X diffraction, only the peak of ANATASU \*\* was accepted, and the diffraction peak based on a zirconium dioxide was not accepted.

[0073] Also in the example 1, the decomposition experiment of an acetic acid was conducted by the same approach by making these fixed photocatalysts into a sample. A result is as being shown in a table 1, and it far exceeded the amount of decomposition of an acetic acid compared with the example 3 (fixed photocatalyst with which a zirconium dioxide exceeds the amount specified by this invention) of a comparison shown below.

[0074] (Example 3 of a comparison) The fixed photocatalyst which uses stainless steel as a base material by the same approach as an example 11 was produced except [ all ] having set the amount of the 2-propanol solution containing (70% of concentration) zirconium tetra-*n*-propoxide to 16.84g. As the photocatalyst (titanium dioxide containing a zirconium dioxide) formed in this base material front face was shown in drawing 2 as a result of an X diffraction, the diffraction pattern based on ANATASU \*\* was not accepted at all.

[0075] Also in the example 1, the decomposition experiment of an acetic acid was conducted by the same approach by making this fixed photocatalyst into a sample. A result is as being shown in a table 1, and most acetic acids were not disassembled. Although this was not observed by the X diffraction, the multiple oxides (ZrTiO<sub>4</sub> etc.) of titanium and a zirconium mainly generate it, and it is because photocatalyst activity decreased remarkably.

[0076] (Example 18) The fixed photocatalyst which uses stainless steel as a base material by the same approach as an example 11 was produced using the sol liquid (Ti/Zr=18-mol%) prepared in the example 16 except [ all ] having set burning temperature into 900 degrees C, and having set firing time as for 3 minutes. The photocatalyst formed in this base material front face consists of microcrystal size 25.5nm ANATASU \*\*, and rutile \*\* was not contained.

[0077] Also in the example 1, the decomposition experiment of an acetic acid was conducted by the same approach by making this fixed photocatalyst into a sample. The result was as being shown in a table 1.

[0078]

[A table 1]

表 1

No.	焼成温度 (℃)	焼成時間 (分)	Zr/Ti (mol%)	TiO <sub>2</sub> 結晶子サイズ (773K, 10s) (nm)	酢酸分解量 (μmol)		
実	1	550	3	—	15.5	80.0	
	2	250	30	—	6.0	54.5	
	3	550	6	—	16.6	59.3	
	4	550	10	—	19.0	32.7	
	5	550	20	—	20.2	18.2	
	6	550	30	—	24.1	5.2	
	7	400	30	—	15.0	82.1	
	8	600	30	—	27.3	1.5	
施	9	500	3	—	13.3	92.1	
	10	800	3	—	28.9	12.0	
	11	550	60	1	20.1	17.7	
	12	500	60	3	20.0	43.0	
	13	550	60	3	19.5	35.5	
	14	550	60	6	24.0	42.0	
	15	550	60	12	22.5	49.5	
	16	550	60	18	23.0	61.3	
例	17	550	60	24	23.5	55.2	
	18	900	3	18	25.5	42.6	
	比較例	1	550	60	—	* 32.5	0.3
	2	* 850	3	—	* 35.5	0	
	例	3	550	60	* 30	* 回折ピーク出ず	0.5

(注) \*印：本発明で規定する範囲から外れることを表す。

[0079] (Example 19) In order to check the deodorization effectiveness of a fixed photocatalyst, the acetaldehyde was assumed to be an offensive odor component and the decomposition experiment was conducted.

[0080] The fixed photocatalyst produced in the example 16 in the reaction cell made from a quartz (100 cc of content volume) was put in, and it connected with the closeout circulation line (350ml of sum total content volume). The optical exposure was performed through the dimming filter and the UV filter (Toshiba UV-31) from 250W ultrahigh pressure mercury lamp, introducing in a system the acetaldehyde (5000 ppm) diluted with air, and circulating it (ultraviolet-rays on-the-strength 15 mW/cm<sup>2</sup>). In addition, the decrement by decomposition of an acetaldehyde was measured using the gas chromatograph connected to the line.

[0081] Consequently, as shown in drawing 3, the acetaldehyde decreased with time and was set to undetectable level (10 ppm or less) after 120 minutes.

[0082] (Example 4 of a comparison) Also in the example 19, the decomposition experiment of an acetaldehyde was conducted by the same approach using the fixed photocatalyst produced in the example 1 of a comparison.

[0083] The residual concentration of the acetaldehyde of 120 minutes after was about 3500 ppm, and there were few amounts of decomposition of an acetaldehyde far compared with an example 19 so that it might be shown for showing a result in drawing 3.

[0084] (Example 20) In order to check the antibacterial effectiveness of a fixed photocatalyst, the bactericidal effect over *Escherichia coli* (*Escherichia coli* W3110 share) was investigated.

[0085] It is the *Escherichia coli* after sterilizing the front face by ethanol 70% beforehand, using as a sample the fixed photocatalyst produced in the example 1. 2.5x10<sup>5</sup> It divided at a time into 0.025ml eight drops 0.2ml (the number of *Escherichia coli*: 5x10<sup>4</sup> individual) of physiological saline included an individual/ml, and they were dropped at the front face. Subsequently, the optical exposure was performed for 15 minutes through the dimming filter and the UV filter (Toshiba UV-35) from the upper part under conditions of 95% of relative humidity using 250W ultrahigh pressure mercury lamp (ultraviolet-rays on-the-strength 1 mW/cm<sup>2</sup>).

[0086] Then, after having flushed the fungus liquid on a sample by 9.8ml of physiological saline, carrying out dilution \*\*\*\* of it at the standard agar medium and cultivating at 35 degrees C for 48 hours, the number of micro organisms was measured by carrying out counting of the grown colony. What trickled the physiological saline which antibacterial assessment is the same conditions and contains Escherichia coli into the base material (SUS304) front face which does not form the titanium dioxide (coating), and carried out the optical exposure for 15 minutes, About what trickled into the front face of the fixed photocatalyst produced in the example 1, and was held to the dark place for 15 minutes, it carried out on the basis of the number of micro organisms (it is  $4.8 \times 10^5$  individual and  $4.7 \times 10^5$ , respectively individual) measured like the above.

[0087] Consequently, the number of survival Escherichia coli is  $1.6 \times 10^3$  by carrying out an optical exposure. It became an individual and antibacterial [ outstanding ] was accepted.

[0088] (Example 21) The fixed photocatalyst which made the titanium dioxide form in a quartz plate front face in the shape of a thin film by the same approach as an example 1 was produced except [ all ] having used the quartz plate (1mm in 4cmx4cm thickness) as a base material. the result of having investigated the crystal structure of this photocatalyst according to the X diffraction -- a titanium dioxide -- ANATASU \*\* -- it changes and that microcrystal size was [ from ] 14.5nm.

[0089] The decomposition experiment of tetrachloroethylene was conducted using this titanium-dioxide fixed photocatalyst as a sample. In addition, tetrachloroethylene is matter which is used as solvents, such as a detergent, a fat, and resin, and is regarded as questionable as one of the contamination factors of an underground water.

[0090] First, after having put 40ml of water solutions of tetrachloroethylene with a concentration of 30 ppm into the reaction cel made from a quartz (100 cc of content volume), dipping the sample into it and carrying out bubbling of the oxygen for 20 minutes, the optical exposure was performed through the UV filter (Toshiba UV- 29) from 250W ultrahigh pressure mercury lamp for 4 hours. Then, the quantum of the amount of the tetrachloroethylene contained in a water solution was carried out using the gas chromatograph. Consequently, the concentration of tetrachloroethylene was decreasing to 3.2 ppm.

[0091] (Example 22) The fixed photocatalyst which made the titanium dioxide form in a paint steel plate front face in the shape of a thin film by the same approach as way \*\*\*\*\* 2 was produced except having made firing time into 2 minutes, using the paint steel plate (1mm in 5cmx5cm thickness) of a resin system as a base material. As a result of an X diffraction's investigating the crystal structure of this photocatalyst, a titanium dioxide consists of ANATASU \*\* and that microcrystal size was 5.8nm.

[0092] The clearance trial of the tar of the tobacco made to adhere to a sample front face in the following ways was performed using this photocatalyst as a sample.

[0093] After making the tar of tobacco 1 duty adhere to a sample front face compulsorily, reduction in tar was evaluated by measuring b value change which serves as a yellow rule of thumb from 250W ultrahigh pressure mercury lamp using a color difference meter while performing an optical exposure (ultraviolet-rays on-the-strength 5 mW/cm<sup>2</sup>) through a dimming filter and a UV filter (Toshiba UV- 35).

[0094] Consequently, b value was set to about 0 by the optical exposure of 16.5 to 2 before an optical exposure hours, and since the color (white) of the paint used also for appearance as a base material revived, it was checked that tar is removed effectively. When the same trial was performed using the paint steel plate which omits the above processings on the other hand, b value was not set to 8.2 by the optical exposure of 13.4 to 2 before an optical exposure hours, but tar remained considerably on the sample front face.

[0095]

[Effect of the Invention] The fixed photocatalyst of this invention has high labile, and the effectiveness which was excellent to decomposition of the harmful matter under atmospheric air or wastewater, the quality of a dirt affix, etc. and clearance is shown. Therefore, if a metal, glass, a ceramic, etc. are used as a base material, members to which the operation effectiveness, such as antibacterial, deodorization, \*\*\*\*, antifungal, and disassembly of an environmental pollutant, was given, such as inner package material and building materials, can be offered easily. Especially, according to the decomposition / clearance approach of the harmful matter of this invention, the harmful matter also including the various quality of an affix which has an adverse effect on the body or has the possibility can be disassembled and removed effectively.

[0096] According to the manufacture approach of this invention, this photocatalyst may not need a special facility and actuation using a comparatively cheap raw material, and its firing time may be short, and it can be manufactured by low cost compared with the conventional fixed photocatalyst.

[Translation done.]

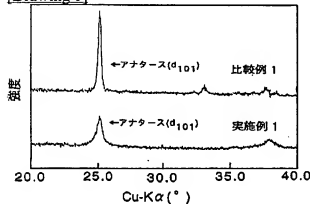
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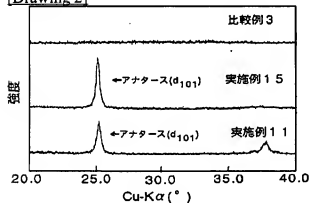
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

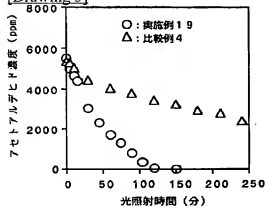
[Drawing 1]



[Drawing 2]



[Drawing 3]





[Translation done.]

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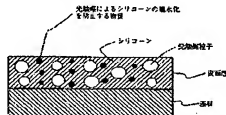
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(54) 発明の名称 外装用塗材

(57) 【要約】

【課題】 長期にわたり撥水性を維持可能であり、汚れにくい外装用塗材の提供。

【解決手段】 外装用塗材において、基材表面に、光触媒粒子と、撥水性シリコンと、前記撥水性シリコンの前記光触媒の光触媒による撥水化を防止するための物質とを含有する表面層が形成されているようにする、或いは基材表面に 光触媒粒子と撥水性シリコンとを含有する層が形成され、さらにその層表面の少なくとも一部には前記撥水性シリコンの前記光触媒の光触媒による撥水化を防止するための物質が固定されているようにする。



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【特許請求の範囲】

【請求項1】 基材表面に、光触媒粒子と、撥水性シリコンと、前記撥水性シリコンの前記光触媒の光触媒による親水化を防止するための物質とを含有する表面層が形成されていることを特徴とする外装用建材。

【請求項2】 基材表面に、光触媒粒子と撥水性シリコンとを含有する層が形成され、さらにその層表面の少なくとも一部には前記撥水性シリコンの前記光触媒の光触媒による親水化を防止するための物質が固定されていることを特徴とする外装用建材。

【請求項3】 前記光触媒の光触媒による親水化を防止するための物質は、コバルト又はコバルト化合物であることを特徴とする請求項1、2に記載の外装用建材。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、煙塵や排気ガスなどの燃焼生成物による汚れや、上方にあるシラントから滴出する汚れや、建物の排気口から排出される汚染物質などで汚れにくい防汚性外装用建材に関する。

【0002】

【従来の技術】高層ビルや住宅等の外壁は、煤塵や排気ガスなどの燃焼生成物による汚れや、上方にあるシラントから滴出する汚れや、建物の排気口から排出される汚染物質などで汚れる。これらの汚れは得易く、建物の美観を著しく損ねる。さらに高層ビル外壁を清掃しようとすれば、その労力は、高所作業であり、重労働であると同時に危険を伴う。

【0003】

【発明が解決しようとする課題】そこで、汚れにくい外装用建材が望まれている。

【0004】汚れの付着を防止する方法としては、基材表面に撥水性を付与するといことが知られている。基材表面に撥水性を付与すると、表面エネルギーが著しく小さくなるため、汚れ成分が付着されにくくなる。その一方として、基材表面に撥水性シリコンからなる表面層を形成する方法がある。しかしながら、この構成では経時的に汚れが付着することによって水との接触角が70°程度に低下し、撥水性の効果が持続しない。そこで、上記課題を解決する他の方法として、基材表面に光触媒と撥水性シリコンとからなる表面層を形成する方法がある。この方法によれば、光触媒の酸化分解性に基づき、経時的に付着する汚れを分解できる。しかしながら、この構成では屋外で太陽光に晒すと、光触媒の光触媒によりシリコンが親水化してしまうため表面の撥水性を維持することができない。本発明では、上記事情に鑑み、表面の撥水性を長期にわたり維持しうる外装用建材を提供し、以て汚れにくい外装用建材を提供することを目的とする。

【0005】

【課題を解決するための手段】本発明では、上記課題を

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解決すべく、基材表面に、光触媒粒子と、撥水性シリコンと、前記撥水性シリコンの前記光触媒の光触媒による親水化を防止するための物質とを含有する表面層が形成されている。或いは基材表面に、光触媒粒子と撥水性シリコンとを含有する層が形成され、さらにその層表面の少なくとも一部には前記撥水性シリコンの前記光触媒の光触媒による親水化を防止するための物質が固定されていることを特徴とする外装用建材を提供する。コバルト又はコバルト化合物のような光触媒の光触媒による親水化を防止するための物質が表面層に含有されているようにすることにより、光触媒の光触媒によりシリコンが親水化してしまうのを防止することができる。かつ光触媒が含有されているので、光触媒の酸化分解性に基づき、経時的に付着する汚れを分解できる。従って、表面の撥水性を維持することができ、外装用建材は恒久的に汚れにくい状態を維持することができる。

【0006】

【発明の実施形態】本発明の一実施形態においては、外装用建材表面には、図1に示すように、光触媒粒子と、シリコンと、コバルト又はコバルト化合物等の光触媒の光触媒による親水化を防止するための物質を含む表面層が形成されている。本発明の他の実施形態においては、外装用建材表面には、図2に示すように、光触媒粒子と、撥水性シリコンとを含有する層が形成され、さらにその層表面の少なくとも一部にはコバルト又はコバルト化合物等の撥水性シリコンの光触媒の光触媒による親水化を防止するための物質が固定されている。外装用建材の基材には、適切な基材である珪酸タイル、無鉛タイル、珪瓦、結晶化ガラス、ガラスブロック、コンクリート、石材、木材、軽質気泡コンクリート、石膏セメントケイ酸カルシウム、プレキャスト鉄筋コンクリート、石膏ボードなどの無機質材；及びその表面に、アクリル樹脂、ウレタン樹脂、ポリエステル、シリコン、フッ素樹脂、アクリルシリコン樹脂などの樹脂塗料を塗した化雑樹脂材；アルミニウム、ステンレス、鉄鋼等の金属基材、及びその表面に、アクリル樹脂、ウレタン樹脂、ポリエステル、シリコン、フッ素樹脂、アクリルシリコン樹脂などの樹脂塗料を塗した塗料被覆材；ポリカーボネート、アクリル等のプラスチック又はその塗料被覆材等が好適に利用される。基材と表面層との間には耐熱性の中間層を設けてもよい。耐熱性の中間層の材質としては、シリコン樹脂、無定形シリカ、アクリルシリコン樹脂等が好適に利用される。

【0007】光触媒とは、その結晶の伝導帯と価電子帯との間のエネルギーギャップよりも大きなエネルギー（すなわち短い波長）の光（励起光）を照射したときに、価電子帯中の電子の励起（光励起）が生じ、伝導帯と正孔を生成しうる物質をいい、例えば、アナターゼ型酸化チタン、酸化亜鉛、酸化亜鉛、酸化亜鉛二酸、三酸



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は、スプレーコーティング法、ディップコーティング法、フローコーティング法、スピンコーティング法、ロールコーティング法、刷毛塗り、スポンジ塗り等の方法が好適に利用できる。硬化方法としては、熱処理、真空放置、紫外線照射等により重合させて行うことができる。

【0020】次に、基材表面に、光触媒粒子と吸水性シリコンとを含有する層が形成され、さらにその層表面の少なくとも一部には前記吸水性シリコンの前記光触媒の光励起による加水分解を防止するための物質が固定されている吸水性部材の製造について説明する。この場合の製造は、基本的には、光触媒粒子と吸水性シリコンの前駆体とを含有するコーティング組成物を塗布し、硬化させた後、コバルト又はコバルト化合物等の光触媒の光励起による加水分解を防止するための物質を含有する層を塗布し、表面に固定することによる。

【0021】ここでコーティング組成物は、光触媒粒子と、吸水性シリコンの前駆体を必須構成要素とし、その他に水、エタノール、プロパノール等の溶媒や、塩酸、硝酸、硫酸、リン酸、マレーン酸等のシリカの前駆体の加水分解を促進する触媒や、トリブチルアミン、ヘキサメチルアミンなどの塩基性化合物類、アルミニウムトリイソプロポキシド、テトライソプロピルチタネートなどの酸性化合物類等のシリカの前駆体を硬化させる触媒や、シランカップリング剤等のコーティング液の分散性を向上させる界面活性剤などを添加してもよい。

【0022】ここでシリコンの前駆体としては、平均組成式



(式中、Rは一価の有機基の1種若しくは2種以上からなる官能基、又は、一価の有機基と水素基から選ばれた2種以上からなる官能基であり、Xはアルコキシ基、又は、ハロゲン原子であり、 $p$ 及び $q$ は $0 < p < 2$ 、 $0 < q < 4$ を満足する数である)で表されるシリコンからなる塗膜形成要素、又は一値式



(式中、Rは一価の有機基の1種若しくは2種以上からなる官能基、又は、一価の有機基と水素基から選ばれた2種以上からなる官能基であり、Xはアルコキシ基、又は、ハロゲン原子であり、 $p$ は1または2である)で表される加水分解性シラン誘導体からなる塗膜形成要素、が好適に利用できる。

【0023】ここで上記加水分解性シラン誘導体からなる塗膜形成要素としては、メチルトリメトキシシラン、メチルトリエトキシシラン、メチルトリプロポキシシラン、メチルトリブトキシシラン、エチルトリメトキシシラン、エチルトリエトキシシラン、エチルトリプロポキシシラン、エチルトリブトキシシラン、フェニルトリメトキシシラン、フェニルトリエトキシシラン、フェニルトリプロポキシシラン、フェニルトリブトキシシラン、

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ジメチルジメトキシシラン、ジメチルジエトキシシラン、ジメチルジプロポキシシラン、ジメチルジブトキシシラン、ジエチルジメトキシシラン、ジエチルジエトキシシラン、ジエチルジプロポキシシラン、ジエチルジブトキシシラン、フェニルメチルジメトキシシラン、フェニルメチルジエトキシシラン、フェニルメチルジプロポキシシラン、フェニルメチルジブトキシシラン、 $n$ -プロピルトリメトキシシラン、 $n$ -プロピルトリエトキシシラン、 $n$ -プロピルトリプロポキシシラン、 $n$ -プロピルトリブトキシシラン、 $\gamma$ -グリコキシドキシプロピルトリメトキシシラン、 $\gamma$ -グリコキシドキシプロピルトリメトキシシラン等が好適に利用できる。

【0024】また上記シリコンからなる塗膜形成要素としては、上記加水分解性シラン誘導体の部分加水分解及び縮水重合、又は上記加水分解性シラン誘導体の部分加水分解物と、テトラメトキシシラン、テトラエトキシシラン、テトラプロポキシシラン、テトラブトキシシラン、ジエチルジメトキシシラン等の部分加水分解物との縮水重合等で作製することができる。

【0025】上記コーティング組成物の塗布方法としては、スプレーコーティング法、ディップコーティング法、フローコーティング法、スピンコーティング法、ロールコーティング法、刷毛塗り、スポンジ塗り等の方法が好適に利用できる。硬化方法としては、熱処理、真空放置、紫外線照射等により重合させて行うことができる。

【0026】コバルト又はコバルト化合物等の光触媒の光励起による加水分解を防止するための物質を含有する層を塗布し、表面に固定する方法は、例えば、塩化コバルト、硫酸コバルト、ヨウ化コバルト、臭化コバルト、硝酸コバルト、塩素酸コバルト、硝酸コバルト等の塩性のコバルト化合物を、スプレーコーティング法、ディップコーティング法、フローコーティング法、スピンコーティング法、ロールコーティング法、刷毛塗り、スポンジ塗り等の方法で塗布し、光触媒、熱処理、アルコール等の塩性酸化剤を併用する還元等の方法で固定することにより行う。

【0027】

【実施例】

参考例、アタカーゼ型酸化チタンゾル(日産化学、TA-1-5、硝酸解離液、 $pH=1$ )と、シリカゾル(日本合成ゴム、グラスカB液、 $pH=4$ )と、メチルトリメトキシシラン(日本合成ゴム、グラスカB液)とエタノールを混合し、2~3時間攪拌して得たコーティング液を、スプレーコーティング法にて $5 \times 10 \text{ cm}$ 角の塩化タイル基材(東海機器、AB02E11)上に塗布し、200℃で15分熱処理して、アタカーゼ型酸化チタン被膜11を形成し、シリカB重曹塗、シリコンB重曹塗からなる表面層を形成した#1試料を得た。#1試料の水との接触角は92°であった。ここで水との接触角は

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接触角測定器（協和界面科学、CA-X150）を用い、マイクロスリッジから水滴を滴下した後30秒後の水との接触角を評価した。次いで、#1試料表面に、紫外線光源（三共電気、ブラックライトブルー（BLB）蛍光灯）を用いて、 $0.3\text{ mW/cm}^2$ の紫外線照度で1日照射し、#2試料を得た。その結果、#2試料の水との接触角は $0^\circ$ まで親水化された。次に、#1試料と、#1試料に水銀粒を $2.2.8\text{ mW/cm}^2$ の紫外線照度で2時間照射して得た#3試料の試料表面をラマン分光分析した。その結果、#1試料表面で認められたメチル基のピークが#3試料では認められず、代わりに水酸基のブロードなピークが認められた。以上のことから、光触媒であるアナターゼ型酸化チタンの光照射により被膜の表面のシリコン分子中のケイ素原子に結合した有機基は、水酸基に置換されること、及び親水化されることがわかる。

【0028】実施例1. アナターゼ型酸化チタンゾル（白濁化、TA-15、前記解離型、 $\text{pH}=1$ ）と、シリカゾル（日本合成ゴム、グラスカA液、 $\text{pH}=4$ ）と、メチルトリメチキシラン（日本合成ゴム、グラスカB液）と、塩化コバルト六水和物と、エタノールを混合し、2〜3時間攪拌して得たコーティング液を、スプレーコーティング法にて $5\times 10\text{ cm}$ 角の絶縁タイル基材（東陽機器、AB02E11）上に塗布し、 $200^\circ\text{C}$ で15分熱処理して、アナターゼ型酸化チタン粒子11重層部、シリカ6重層部、シリコン5重層部、コバルト0.2重層部からなる表面層を形成した#4試料を得た。#4試料の水との接触角は $97^\circ$ であった。ここで水との接触角は接触角測定器（協和界面科学、CA-X150）を用い、マイクロスリッジから水滴を滴下した後30秒後の水との接触角で評価した。次いで#4試料表面に、紫外線光源（三共電気、ブラックライトブルー（BLB）蛍光灯）を用いて、 $0.3\text{ mW/cm}^2$ の紫外線照度で1日照射し、#5試料を得た。その結果、#5試料の水との接触角は依然 $96^\circ$ と撥水性を維持した。従って、以上のことから、光触媒であるアナターゼ型酸化チタンの光照射による被膜の表面のシリコンの親水化が、コバルトにより阻害されることがわかる。これは、被膜の表面のシリコン分子中のケイ素原子に結合した有機基の水酸基への置換がコバルトにより阻害されるためと考えられる。

【0029】実施例2. アナターゼ型酸化チタンゾル（白濁化、TA-15、前記解離型、 $\text{pH}=1$ ）と、シリカゾル（日本合成ゴム、グラスカA液、 $\text{pH}=4$ ）と、メチルトリメチキシラン（日本合成ゴム、グラスカB液）と、エタノールを混合し、2〜3時間攪拌して得たコーティング液を、スプレーコーティング法にて5

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$10\text{ cm}$ 角の絶縁タイル基材（東陽機器、AB02E11）上に塗布し、 $200^\circ\text{C}$ で15分熱処理して、アナターゼ型酸化チタン粒子11重層部、シリカ6重層部、シリコン5重層部からなる表面層を形成した。さらにその上にコバルト金属濃度 $50\text{ mmol/L}$ の塩化コバルト六水和物水溶液を、0.3g塗布後、紫外線光源（三共電気、ブラックライトブルー（BLB）蛍光灯）を用いて紫外線照度 $0.4\text{ mW/cm}^2$ の紫外線を10分照射して基材上にコバルトを固定して#6試料を得た。#6試料の水との接触角は $95^\circ$ であった。ここで水との接触角は接触角測定器（協和界面科学、CA-X150）を用い、マイクロスリッジから水滴を滴下した後30秒後の水との接触角で評価した。次いで#6試料表面に、紫外線光源（三共電気、ブラックライトブルー（BLB）蛍光灯）を用いて、 $0.3\text{ mW/cm}^2$ の紫外線照度で1日照射し、#7試料を得た。その結果、#7試料の水との接触角は依然 $94^\circ$ と撥水性を維持した。従って、以上のことから、光触媒であるアナターゼ型酸化チタンの光照射による被膜の表面のシリコンの親水化が、コバルトにより阻害されることがわかる。これは、被膜の表面のシリコン分子中のケイ素原子に結合した有機基の水酸基への置換がコバルトにより阻害されるためと考えられる。

【0030】実施例3. #5試料、#7試料、及び比較のためポリテトラフルオロエチレン被覆を被膜の裏上の置換部分の下に図3のように設け、4か月放置した。その結果、ポリテトラフルオロエチレン被覆では汚れが観察されたのに対し、#5試料、#7試料では汚れは観察されなかった。

【0031】

【発明の効果】本発明では、外壁用建材において、基材表面に、光触媒粒子と、撥水性シリコンと、前記撥水性シリコンの前記光触媒の光照射による親水化を防止するための物質とを含有する表面層が形成されているようにする、或いは基材表面に、光触媒粒子と撥水性シリコンとを含有する層が形成され、さらにその層表面の少なくとも一部に前記撥水性シリコンの前記光触媒の光照射による親水化を防止するための物質が固定されているようにすることにより、部材表面は長期にわたり撥水性を維持可能となり、以て恒久的に汚れにくくなる。

【図面の簡単な説明】

【図1】本発明に係る外壁用建材の表面構造を示す図。

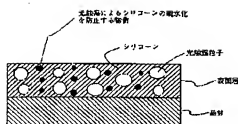
【図2】本発明に係る外壁用建材の断面構造面を示す図。

【図3】本発明の実施例に係る試験の試料の設置方法を示す図。

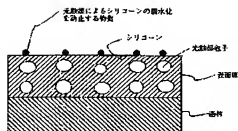
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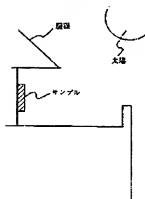
【図1】



【図2】



【図3】



フロントページの続き

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発明の要旨

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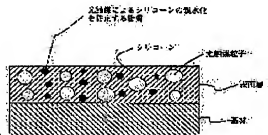
(72)Inventor : KITAMURA ATSUSHI  
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## (54) BUILDING MATERIAL FOR EXTERNAL WALL

## (57)Abstract:

PROBLEM TO BE SOLVED: To keep the water-repellent property of a surface and prevent the surface from getting dirty, by forming a surface layer containing photocatalyst particles, water-repellent silicone, and a substance preventing the water-repellent silicone from getting hydrophilic owing to the photoexcitation of the photocatalyst, on a base material surface.

SOLUTION: A surface layer containing photocatalyst particles such as anatase type titanium oxide, zinc oxide, tin oxide, water-repellent silicone, a substance such as cobalt or cobalt compounds preventing the water-repellent silicone from getting hydrophilic owing to the photoexcitation of the photocatalyst, is formed on the base material surface of a building material for an external wall such as glazed tiles, non-glazed tiles, bricks. Cobalt alloy, cobalt oxide, etc., are favorable for cobalt compounds and the film thickness of the surface layer is favorably made 0.4 $\mu$ m or thinner. In this way, white turbidity resulting from diffuse reflection of light can be prevented and the surface layer becomes substantially transparent. And further, color development of the surface layer resulting from interference of light can be prevented by making the film thickness 0.2 $\mu$ m or thinner.



## LEGAL STATUS

[Date of request for examination]

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[Date of final disposal for application]

[Patent number]

[Date of registration]



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**CLAIMS**

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[Claim(s)]

[Claim 1] Building materials for outer walls characterized by forming the surface layer containing a photocatalyst particle, water-repellent silicone, and the matter for preventing the hydrophilization by optical pumping of said photocatalyst of said water-repellent silicone in a base material front face.

[Claim 2] Building materials for outer walls characterized by forming the layer containing a photocatalyst particle and water-repellent silicone in a base material front face, and fixing the matter for preventing the hydrophilization by optical pumping of said photocatalyst of said water-repellent silicone to a part of the layer front face [ at least ] further.

[Claim 3] The matter for preventing the hydrophilization by optical pumping of said photocatalyst is the building materials for outer walls given in claims 1 and 2 characterized by being cobalt or a cobalt compound.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to dirt at the building materials for pile antifouling property outer walls with the dirt by products of combustion, such as soot dust and exhaust gas, the dirt eluted from the sealant in the upper part, the pollutant discharged from the exhaust port of a building.

[0002]

[Description of the Prior Art] The outer wall of a skyscraper, a residence, etc. becomes dirty with the dirt by products of combustion, such as soot dust and exhaust gas, the dirt eluted from the sealant in the upper part, the pollutant discharged from the exhaust port of a building. These dirt is dark and spoils the fine sight of a building remarkably. If it is furthermore going to clean a skyscraper outer wall, the cleaning is the operation in height, and while it is hard work, it will be accompanied by risk.

[0003]

[Problem(s) to be Solved by the Invention] Then, dirt is expected the building materials for pile outer walls.

[0004] It is known that it is good to give water repellence to a base material front face as an approach of preventing adhesion of dirt. If water repellence is given to a base material front face, since surface energy will become remarkably small, a dirt component becomes being hard to adhere. There is the approach of on the other hand forming in a base material front face as law the surface layer which consists of water-repellent silicone. However, with this configuration, when dirt adheres with time, a contact angle with water falls to about 70 degrees, and water-repellent effectiveness does not continue. Then, there is the approach of forming in a base material front face the surface layer which consists of a photocatalyst and water-repellent silicone as other approaches of solving the above-mentioned technical problem. According to this approach, the dirt which adheres with time can be disassembled based on the oxidative degradation nature of a photocatalyst. However, with this configuration, if it exposes to sunlight outdoors, since silicone carries out hydrophilization by optical pumping of a photocatalyst, surface water repellence is unmaintainable. It aims at offering the building materials for outer walls which can carry out rear-spring-supporter maintenance of the surface water repellence at a long period of time in view of the above-mentioned situation, with providing dirt with the building materials for pile outer walls in this invention.

[0005]

[Means for Solving the Problem] In this invention, on a base material front face, that the above-mentioned technical problem should be solved A photocatalyst particle and water-repellent silicone, The surface layer containing the matter for preventing the hydrophilization by optical pumping of said photocatalyst of said water-repellent silicone is formed. Or the layer containing a photocatalyst particle and water-repellent silicone is formed in a base material front face, and a part of the layer front face [ at least ] is further provided with the building materials for outer walls characterized by fixing the matter for preventing the hydrophilization by optical pumping of said photocatalyst of said water-repellent silicone. When making it the matter for preventing the hydrophilization by optical pumping of a photocatalyst like cobalt or a cobalt compound contain in the surface layer, it can prevent that silicone carries out hydrophilization by optical pumping of a photocatalyst. And since the photocatalyst contains, the dirt which adheres with time can be disassembled based on the oxidative degradation nature of a photocatalyst. Therefore, surface water repellence can be maintained and the building materials for outer walls can maintain a pile condition to dirt everlastingly.

[0006]

[Embodiment of the Invention] In one embodiment of this invention, as shown in drawing 1 , the surface layer containing the matter for preventing the hydrophilization by optical pumping of photocatalysts, such as

a photocatalyst particle, silicone, and cobalt or a cobalt compound, is formed in the building-materials front face for outer walls. In other modes of this invention, the layer which contains a photocatalyst particle and water-repellent silicone as shown in drawing 2 is formed in the building-materials front face for outer walls, and the matter for preventing the hydrophilization by optical pumping of the photocatalyst of water-repellent silicone, such as cobalt or a cobalt compound, is being further fixed to a part of the layer front face [ at least ]. The glazed tile, unglazed tile which are well-known building materials at the base material of the building materials for outer walls, Brick, crystallization glass, a glass block, concrete, a stone, timber, Autoclaved lightweight concrete, an asbestos-cement calcium silicate, precast reinforced concrete, On inorganic base material [ , such as an asbestos cement sheet, pulp cement, and plaster board, ]; and its surface Acrylic resin, urethane resin, polyester, silicone, a fluoro resin, Makeup inorganic building materials which painted plastic paint, such as acrylic silicon resin; Aluminum, On metal bases, such as stainless steel and steel, and the surface of those, acrylic resin, urethane resin, Paint steel plate material which painted plastic paint, such as polyester, silicone, a fluoro resin, and acrylic silicon resin; plastics or its paint plates, such as a polycarbonate and an acrylic, etc. can use suitably. A corrosion-resistant interlayer may be prepared between a base material and a surface layer. As a corrosion-resistant interlayer's construction material, silicone resin, a non-fixed form silica, acrylic silicone resin, etc. can use suitably.

[0007] When the light (excitation light) of energy (namely, short wavelength) with a bigger photocatalyst than the energy gap between the conduction band of the crystal and a valence band is irradiated, excitation (optical pumping) of the electron in a valence band arises, and conduction electron and the matter which can generate an electron hole are said, for example, oxides, such as anatase mold titanium oxide, a zinc oxide, tin oxide, ferric oxide, bismuth(III) oxide, a tungstic trioxide, and strontium titanate, can use suitably. As the light source used for optical pumping of a photocatalyst, since it is exposed to the sun in the daytime, sunlight can be used.

[0008] The resin expressed with average empirical formula  $RpSiO(4-p)/2$  (R is the functional group which consists of one sort of the organic radical of monovalence or two sorts or more, or a functional group which consists of two or more sorts chosen from the organic radical and hydrogen radical of monovalence among a formula, X is an alkoxy group or a halogen atom, and p is a number with which are satisfied of  $0 < p < 2$ ) can be used for silicone.

[0009] A cobalt alloy, cobalt oxide, a cobalt chloride, cobalt sulfate, a cobalt iodide, a cobalt bromide, cobaltous acetate, chloric-acid cobalt, a cobalt nitrate, etc. can use for a cobalt compound suitably.

[0010] As for the thickness of a surface layer, it is desirable to make it 0.4 micrometers or less. Then, nebula by the scattered reflection of light can be prevented and a surface layer serves as transparency substantially. When thickness of a surface layer is set to 0.2 micrometers or less, it is much more more desirable still. Then, coloring of the surface layer by interference of light can be prevented. Moreover, the more a surface layer is thin, the more the transparency improves. Furthermore, if thickness is made thin, the abrasion resistance of a surface layer will improve.

[0011] A metal like Ag, Cu, and Zn can be added in a surface layer. The surface layer which added said metal can annihilate the bacteria and mold adhering to a front face even in a dark place.

[0012] To a surface layer, a platinum metal like Pt, Pd, Ru, Rh, Ir, and Os can be added. The surface layer which added said metal can reinforce the oxidation reduction activity of a photocatalyst, and can raise the resolvability of organic substance dirt, and the resolvability of a harmful gas or an offensive odor.

[0013] Next, the process of the water-repellent member by which the surface layer containing a photocatalyst particle, water-repellent silicone, and the matter for preventing the hydrophilization by optical pumping of said photocatalyst of said water-repellent silicone is formed in the base material front face is explained. Fundamentally, the process in this case is based on making a base material front face apply and harden a coating constituent.

[0014] A coating constituent makes the precursor of silicone the requirements for an indispensable configuration here at the matter for preventing the hydrophilization by optical pumping of photocatalysts, such as a photocatalyst particle, cobalt, or a cobalt compound. In addition, solvents, such as water, ethanol, and propanol, a hydrochloric acid and a nitric acid, a sulfuric acid, The catalyst which promotes hydrolysis of the precursor of silicone, such as an acetic acid and a maleic acid, Basic compounds, such as tributylamine and hexylamine, aluminum TORIISO propoxide, The catalyst which stiffens the precursor of silicone, such as acid compounds, such as tetra-isopropyl titanate, the surfactant which raises the dispersibility of coating liquid, such as a silane coupling agent, may be added.

[0015] As cobalt or a cobalt compound, it is desirable to use a water-soluble cobalt compound. As a water-soluble cobalt compound, a cobalt chloride, cobalt sulfate, a cobalt iodide, a cobalt bromide, cobaltous

acetate, chloric-acid cobalt, a cobalt nitrate, etc. can use suitably, for example.

[0016] here -- as the precursor of silicone -- the average empirical formula  $RpSiXqO(4-p-q)/2$  (the functional group which R becomes from one sort of the organic radical of monovalence, or two sorts or more among a formula --) It is the functional group which consists of two or more sorts chosen from the organic radical and hydrogen radical of monovalence. X Or an alkoxy group, or the number with which it is a halogen atom and p and q are satisfied of  $0 < p < 2$  and  $0 < q < 4$  -- it is -- the film-forming material which consists of a siloxane expressed -- or general formula  $RpSiX4-p$  (the functional group which R becomes from one sort of the organic radical of monovalence, or two sorts or more among a formula --) or the functional group which consists of two or more sorts chosen from the organic radical and hydrogen radical of monovalence -- it is -- X -- an alkoxy group or a halogen atom -- it is -- p -- 1 or 2 -- it is -- film-forming-material \*\* which consists of a hydrolysis nature silane derivative expressed can use suitably.

[0017] As a film-forming material which consists of the above-mentioned hydrolysis nature silane derivative here Methyl trimethoxysilane, methyl triethoxysilane, a methyl tripropoxy silane, MECHIRUTORI butoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, An ethyl tripropoxy silane, ECHIRUTORI butoxysilane, phenyltrimethoxysilane, Phenyltriethoxysilane, a phenyl tripropoxy silane, a phenyl TORIBUTOKI gardenia fruit run, Dimethyl dimethoxysilane, dimethyl diethoxysilane, a dimethyl dipropoxy silane, Dimethyl dibutoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, A diethyl dipropoxy silane, diethyl dibutoxysilane, phenylmethyl dimethoxysilane, Phenylmethyl diethoxysilane, a phenylmethyl dipropoxy silane, Phenylmethyl dibutoxysilane, n-propyl trimethoxysilane, n-propyl triethoxysilane, n-propyl tripropoxy silane, n-pro PIRUTORI butoxysilane, gamma-glycoxyde KISHIPURO pill trimethoxysilane, gamma-acryloxypropyltrimethoxysilane, etc. can use suitably.

[0018] Moreover, as a film-forming material which consists of the above-mentioned siloxane, it is producible by the dehydration condensation polymerization of the partial hydrolysate of the partial hydrolysis of the above-mentioned hydrolysis nature silane derivative and dehydration condensation polymerization, or the above-mentioned hydrolysis nature silane derivative, and partial hydrolysates, such as a tetramethoxy silane, a tetra-ethoxy silane, tetra-propoxysilane, tetra-butoxysilane, and diethoxy dimethoxysilane, etc.

[0019] As the method of application of the above-mentioned coating constituent, approaches, such as a spray coating method, the DIPPUKO-TINGU method, the flow coating method, the SUPINKO-TINGU method, the roll coating method, brush coating, and sponge coating, can use suitably. As the hardening approach, it can carry out by carrying out a polymerization by heat treatment, room temperature neglect, UV irradiation, etc.

[0020] Next, the layer containing a photocatalyst particle and water-repellent silicone is formed in a base material front face, and the process of the water-repellent member to which the matter for preventing the hydrophilization by optical pumping of said photocatalyst of said water-repellent silicone is being fixed is further explained to a part of the layer front face [ at least ]. Fundamentally, after the process in this case applies and stiffens the coating constituent containing a photocatalyst particle and the precursor of water-repellent silicone, it applies the solution containing the matter for preventing the hydrophilization by optical pumping of photocatalysts, such as cobalt or a cobalt compound, and twists it to fix to a front face.

[0021] A coating constituent makes a photocatalyst particle and the precursor of water-repellent silicone the requirements for an indispensable configuration here. In addition, solvents, such as water, ethanol, and propanol, a hydrochloric acid and a nitric acid, a sulfuric acid, The catalyst which promotes hydrolysis of the precursor of silicas, such as an acetic acid and a maleic acid, Basic compounds, such as tributylamine and hexylamine, aluminum TORIISO propoxide, The catalyst which stiffens the precursor of silicas, such as acid compounds, such as tetra-isopropyl titanate, the surfactant which raises the dispersibility of coating liquid, such as a silane coupling agent, may be added.

[0022] here -- as the precursor of silicone -- the average empirical formula  $RpSiXqO(4-p-q)/2$  (the functional group which R becomes from one sort of the organic radical of monovalence, or two sorts or more among a formula --) It is the functional group which consists of two or more sorts chosen from the organic radical and hydrogen radical of monovalence. X Or an alkoxy group, or the number with which it is a halogen atom and p and q are satisfied of  $0 < p < 2$  and  $0 < q < 4$  -- it is -- the film-forming material which consists of a siloxane expressed -- or general formula  $RpSiX4-p$  (the functional group which R becomes from one sort of the organic radical of monovalence, or two sorts or more among a formula --) or the functional group which consists of two or more sorts chosen from the organic radical and hydrogen radical of monovalence -- it is -- X -- an alkoxy group or a halogen atom -- it is -- p -- 1 or 2 -- it is -- film-forming-material \*\* which consists of a hydrolysis nature silane derivative expressed can use suitably.

[0023] As a film-forming material which consists of the above-mentioned hydrolysis nature silane derivative here Methyl trimethoxysilane, methyl triethoxysilane, a methyl tripropoxy silane, MECHIRUTORI butoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, An ethyl tripropoxy silane, ECHIRUTORI butoxysilane, phenyltrimethoxysilane, Phenyltriethoxysilane, a phenyl tripropoxy silane, a phenyl TORIBUTOKI gardenia fruit run, Dimethyl dimethoxysilane, dimethyl diethoxysilane, a dimethyl dipropoxy silane, Dimethyl dibutoxysilane, diethyl dimethoxysilane, diethyl diethoxysilane, A diethyl dipropoxy silane, diethyl dibutoxysilane, phenylmethyl dimethoxysilane, Phenylmethyl diethoxysilane, a phenylmethyl dipropoxy silane, Phenylmethyl dibutoxysilane, n-propyl trimethoxysilane, n-propyl triethoxysilane, n-propyl tripropoxy silane, n-pro PIRUTORI butoxysilane, gamma-glycoxyde KSHIPURO pill trimethoxysilane, gamma-acryloxypropyltrimethoxysilane, etc. can be used suitably.

[0024] Moreover, as a film-forming material which consists of the above-mentioned siloxane, it is producible by the dehydration condensation polymerization of the partial hydrolysate of the partial hydrolysis of the above-mentioned hydrolysis nature silane derivative and dehydration condensation polymerization, or the above-mentioned hydrolysis nature silane derivative, and partial hydrolysates, such as a tetramethoxy silane, a tetra-ethoxy silane, tetra-propoxysilane, tetra-butoxysilane, and diethoxy dimethoxysilane, etc.

[0025] As the method of application of the above-mentioned coating constituent, approaches, such as a spray coating method, the DIPPUKO-TINGU method, the flow coating method, the SUPINKO-TINGU method, the roll coating method, brush coating, and sponge coating, can be used suitably. As the hardening approach, it can carry out by carrying out a polymerization by heat treatment, room temperature neglect, UV irradiation, etc.

[0026] The approach of applying the solution containing the matter for preventing the hydrophilization by optical pumping of photocatalysts, such as cobalt or a cobalt compound, and fixing to a front face For example, a cobalt chloride, cobalt sulfate, a cobalt iodide, a cobalt bromide, Water-soluble cobalt compounds, such as cobaltous acetate, chloric-acid cobalt, and a cobalt nitrate A spray coating method, the DIPPUKO-TINGU method, the flow coating method, It applies by approaches, such as the SUPINKO-TINGU method, the roll coating method, brush coating, and sponge coating, and carries out by fixing by approaches, such as reduction which uses together sacrifice oxidizers, such as photoreduction, heat treatment, and alcohol.

[0027]

[Example]

An example of reference . anatase mold titanium oxide sol (the Nissan chemistry, TA-15, a nitric-acid amalgam-decomposition mold, pH=1), a silica sol (Japan Synthetic Rubber, GURASUKA A liquid, pH=4) and methyl trimethoxysilane (Japan Synthetic Rubber --) Mix ethanol with GURASUKA B liquid, and apply the coating liquid which agitated for 2 to 3 hours and was obtained with a spray coating method on the glazed-tile base material (TOTO, AB 02E11) of 5x10cm angle, and it is heat-treated at 200 degrees C for 15 minutes. #1 sample in which the surface layer which consists of the anatase mold titanium oxide particle 11 weight section, the silica 6 weight section, and the silicone 5 weight section was formed was obtained. # The contact angle with the water of one sample was 92 degrees. Using the contact angle measuring instrument (consonance interface science, CA-X150), after the contact angle with water trickled waterdrop from the micro syringe, the contact angle with the water of 30 seconds after estimated it here. Subsequently, the ultraviolet-rays light source (the Sankyo electrical and electric equipment, black light bull-(BLB) fluorescent lamp) was used for #1 sample front face, it irradiated with the ultraviolet-rays illuminance of 0.3 mW/cm2 on the 1st, and #2 sample was obtained. Consequently, hydrophilization of the contact angle with the water of #2 sample was carried out to 0 degree. Next, Raman spectroscopic analysis of the sample front face of #1 sample and each #3 sample which irradiated the mercury-vapor lamp for 2 hours, and obtained it with the ultraviolet-rays illuminance of 22.8 mW/cm2 in #1 sample was carried out. Consequently, the peak of a methyl group accepted on #1 sample front face was not accepted by #3 sample, but the broadcloth hydroxyl group peak was accepted instead. It turns out that the organic radical combined with the silicon atom in the silicone molecule of the front face of a coat from the above thing by optical pumping of the anatase mold titanium oxide which is a photocatalyst is permuted by the hydroxyl group, and that hydrophilization is carried out.

[0028] An example 1. anatase mold titanium oxide sol (the Nissan chemistry, TA-15, a nitric-acid amalgam-decomposition mold, pH=1), A silica sol (Japan Synthetic Rubber, GURASUKA A liquid, pH=4) and methyl trimethoxysilane (Japan Synthetic Rubber, GURASUKA B liquid), The coating liquid which mixed ethanol with cobalt chloride 6 hydrate, agitated for 2 to 3 hours, and was obtained Apply with a spray

coating method on the glazed-tile base material (TOTO, AB 02E11) of 5x10cm angle, and it heat-treats at 200 degrees C for 15 minutes. #4 sample in which the surface layer which consists of the anatase mold titanium oxide particle 11 weight section, the silica 6 weight section, the silicone 5 weight section, and the cobalt 0.2 weight section was formed was obtained. # The contact angle with the water of four samples was 97 degrees. Using the contact angle measuring instrument (consonance interface science, CA-X150), after the contact angle with water trickled waterdrop from the micro syringe, the contact angle with the water of 30 seconds after estimated it here. Subsequently, the ultraviolet-rays light source (the Sankyo electrical and electric equipment, black light bull-(BLB) fluorescent lamp) was used for #4 sample front face, it irradiated with the ultraviolet-rays illuminance of 0.3 mW/cm<sup>2</sup> on the 1st, and #5 sample was obtained. Consequently, the contact angle with the water of #5 sample still maintained 96 degrees and water repellence. Therefore, it turns out that the hydrophilization of the silicone of the front face of the coat by optical pumping of the anatase mold titanium oxide which is a photocatalyst is prevented from the above thing with cobalt. This is considered because the permutation to the hydroxyl group of the organic radical combined with the silicon atom in the silicone molecule of the front face of a coat is checked with cobalt.

[0029] An example 2. anatase mold titanium oxide sol (the Nissan chemistry, TA-15, a nitric-acid amalgam-decomposition mold, pH=1), A silica sol (Japan Synthetic Rubber, GURASUKA A liquid, pH=4) and methyl trimetoxysilane (Japan Synthetic Rubber, GURASUKA B liquid), Mix ethanol, and apply the coating liquid which agitated for 2 to 3 hours and was obtained with a spray coating method on the glazed-tile base material (TOTO, AB 02E11) of 5x10cm angle, and it is heat-treated at 200 degrees C for 15 minutes. The surface layer which consists of the anatase mold titanium oxide particle 11 weight section, the silica 6 weight section, and the silicone 5 weight section was formed. Furthermore, after 0.3g spreading and the ultraviolet-rays light source (the Sankyo electrical and electric equipment, black light bull-(BLB) fluorescent lamp) were used for the cobalt chloride 6 hydrate water solution of cobalt metal concentration mol/g of 50micro, the ultraviolet rays of 2 were irradiated the ultraviolet-rays illuminance of 0.4mW/cm on it, for 10 minutes, cobalt was fixed on the base material, and #6 sample was obtained. # The contact angle with the water of six samples was 95 degrees. Using the contact angle measuring instrument (consonance interface science, CA-X150), after the contact angle with water trickled waterdrop from the micro syringe, the contact angle with the water of 30 seconds after estimated it here. Subsequently, the ultraviolet-rays light source (the Sankyo electrical and electric equipment, black light bull-(BLB) fluorescent lamp) was used for #6 sample front face, it irradiated with the ultraviolet-rays illuminance of 0.3 mW/cm<sup>2</sup> on the 1st, and #7 sample was obtained. Consequently, the contact angle with the water of #7 sample still maintained 94 degrees and water repellence. Therefore, it turns out that the hydrophilization of the silicone of the front face of the coat by optical pumping of the anatase mold titanium oxide which is a photocatalyst is prevented from the above thing with cobalt. This is considered because the permutation to the hydroxyl group of the organic radical combined with the silicon atom in the silicone molecule of the front face of a coat is checked with cobalt.

[0030] For example 3.#5 sample, #7 sample, and the comparison, the polytetrafluoroethylene plate was installed like drawing 3 in the bottom of the part with a roof of the roof of a building, and was left for four months. Consequently, by #5 sample and #7 sample, dirt was not observed to dirt having been observed with the polytetrafluoroethylene plate.

[0031]

[Effect of the Invention] In this invention, it sets to the building materials for outer walls. On a base material front face A photocatalyst particle and water-repellent silicone. The surface layer containing the matter for preventing the hydrophilization by optical pumping of said photocatalyst of said water-repellent silicone is formed. Or the layer containing a photocatalyst particle and water-repellent silicone is formed in a base material front face. By furthermore fixing the matter for preventing the hydrophilization by optical pumping of said photocatalyst of said water-repellent silicone to a part of the layer front face [ at least ], maintenance of rear-spring-supporter water repellence of a member front face is attained at a long period of time, with it dirt-comes to be hard of a front face everlastingly.

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[Translation done.]

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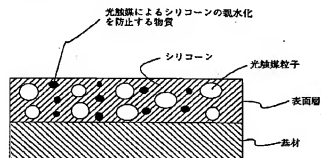
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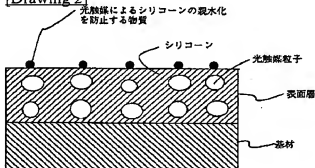
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## DRAWINGS

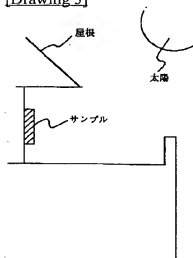
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]



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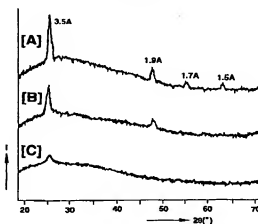
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## (54) Photocatalytic glass pane and method for producing same

(57) The invention relates to a photocatalytic glass pane including a glass substrate and at least one layer formed on at least one major surface of the glass substrate. The at least one layer has an outermost layer made of a photocatalytic titanium oxide. The outermost layer is prepared by a chemical vapor deposition. The titanium oxide is such that an X-ray diffraction chart of the titanium oxide has at least a first peak when a spacing between adjacent crystallographic planes of the titanium oxide is 3.5 angstroms and a second peak when a spacing between adjacent crystallographic planes of the titanium oxide is 1.9 angstroms and that the second peak has a height that is at least one-tenth of a height of the first peak. The glass pane is high in photocatalytic activity. The invention further relates to a method for producing the photocatalytic glass pane. This method has the sequential steps of (a) providing a gas mixture comprising a vapor of an organic titanium compound and an oxygen gas; and (b) bringing the gas mixture into contact with the glass substrate that is under a heated condition, thereby to form the outermost layer on the glass substrate. The glass pane can easily be produced by the method with high efficiency and low cost.

FIG.2



## Description

**BACKGROUND OF THE INVENTION**

[0001] The present invention relates to a photocatalytic glass pane having a photocatalytic titanium oxide layer formed on a glass substrate thereof and a method for producing the glass pane.

[0002] Hitherto, titanium oxide films have been used for providing substrates (e.g. of glass, ceramics and resins) with reflection of heat rays and the like, abrasion resistance, heat resistance, weather resistance and chemical resistance, due to their superior characteristics such as high refractive index, high hardness, heat resistance and chemical resistance. Furthermore, much attention has been drawn in recent years to the photocatalytic activity of titanium oxide to oxidatively decompose organic contaminants.

[0003] There are several ways to form a titanium oxide film on a substrate. For example, in a spraying method, a titanium compound solution is sprayed onto a substrate and then pyrolyzed to form thereon a titanium oxide film. In a sol-gel process, a titania precursor sol is applied to a substrate, and then the resultant precursory film is heated to form thereon a titanium oxide film. In a chemical vapor deposition (CVD), a vapor of an organic titanium compound is brought into contact with a substrate that is under a heated condition, thereby to form thereon a titanium oxide film by pyrolysis.

[0004] Japanese Patent Second Publications JP-B-1-30771 and JP-B-57-47137 disclose methods for producing heat reflective glass panes. In each of these methods, a particular titanium compound solution is sprayed onto a heated glass substrate, thereby to form thereon a titanium oxide film by pyrolysis. Japanese Patent First Publication JP-A-9-59041 discloses an antifogging coating composition containing therein semiconductor photocatalyst particles that are most preferably titania particles. This composition is a dispersion in which (1) a silicone precursor or amorphous silica precursor and (2) semiconductor photocatalyst particles are uniformly dispersed in a solvent. JP-A-9-920 discloses a titanium oxide film that is sufficient in transparency. This film is formed on a substrate by spraying an ethanol solution containing 20 wt% of di-iso-propoxybis(acetylacetonato)titanium.

**SUMMARY OF THE INVENTION**

[0005] It is an object of the present invention to provide a photocatalytic glass pane that is high in photocatalytic activity and superior in optical and physical characteristics such as heat reflection.

[0006] It is another object of the present invention to easily produce such a photocatalytic glass pane with high efficiency and low cost by forming at least one layer on at least one major surface of a glass substrate, while maintaining transparency, flatness and smoothness of the glass substrate.

[0007] According to the present invention, there is provided a photocatalytic glass pane comprising a glass substrate; and at least one layer formed on at least one major surface of the glass substrate. The at least one layer has an outermost layer made of a photocatalytic titanium oxide. The outermost layer is prepared by chemical vapor deposition. The titanium oxide is such that an X-ray diffraction chart (pattern) of the titanium oxide has at least a first peak when a spacing between adjacent crystallographic planes (i.e., an interplanar spacing) of the titanium oxide is 3.5 angstroms (Å) and a second peak when a spacing between adjacent crystallographic planes of the titanium oxide is 1.9 angstroms and that the second peak has a height that is at least one-tenth of a height of the first peak. As is commonly known, the peak height represents the intensity (I) of the diffracted X-rays (see Figs. 2-3). The glass pane is high in photocatalytic activity and superior in optical and physical characteristics such as heat reflection.

[0008] According to the present invention, there is provided a method for producing the above-mentioned photocatalytic glass pane. This method comprises the sequential steps of (a) providing a gas mixture comprising a vapor of an organic titanium compound and an oxygen gas; and (b) bringing the gas mixture into contact with the glass substrate that is under a heated condition, thereby to form the outermost layer on the glass substrate. The organic titanium compound may be titanium alkoxide selected from titanium tetraisopropoxide, titanium tetramethoxide, titanium tetraethoxide, and titanium monochlorotrialkoxide. The gas mixture may further comprise nitrogen gas. The glass pane can easily be produced by the method with high efficiency and low cost, while the glass substrate is maintained in transparency, flatness and smoothness.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0009]

Fig. 1 is a schematic side sectional view showing a float glass production line equipped with a nozzle for forming a titanium oxide film on a glass plate by CVD;

Fig. 2 is an X-ray diffraction chart showing X-ray diffraction patterns [A], [B] and [C] according to Examples 1 and 2 and Comparative Example 1, respectively; and

Fig. 3 is an X-ray diffraction chart of an anatase-type titanium oxide powder that is adherent to a glass substrate by a bonding agent.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] In the invention, the outermost layer (i.e., a titanium oxide film) of the photocatalytic glass pane may be subjected to an X-ray diffraction analysis with CuK  $\alpha$  X-rays produced by an output voltage of 10-80 kV and an electric current of 100-1,000 mA, a scanning speed of up to 10 degrees per minute, a diverging slit's opening angle of 1/2 degrees, and a scattering slit's opening angle of 1/2 degrees.

[0011] As mentioned above, the gas mixture comprising a vapor of an organic titanium compound may be brought into contact with a heated glass substrate (e.g., soda-lime float glass plate), during a float glass production (see Fig. 1). In other words, the outermost titanium oxide layer may be formed on a glass substrate by CVD, particularly under normal pressure (atmospheric pressure). With this, it becomes possible to make the photocatalytic glass pane of the invention to have good transparency, flatness and smoothness, which are inherent in glass itself. It is preferable to conduct the above-mentioned step (b) at a temperature not higher than 750°C. If the temperature is higher than 750°C, the glass substrate may be deformed during the step (b). Furthermore, the outermost layer may have cracks and/or wrinkles on its surface. As is seen from Fig. 1, the step (b) may be conducted in a float glass production line 1. In this line 1, a heated glass substrate 2 from a tin bath 3 is allowed to enter into an annealing chamber 4. It is optional to dispose a nozzle 5, which has a discharge slit 6 for discharging the gas mixture of the step (a) and exhaust slits 7 for exhausting the gas mixture, in the vicinity of the entrance of the annealing chamber 4, as illustrated. In fact, it is preferable to dispose the nozzle 5 in a region of the production line 1 that is at least 5 m downstream from the end top roller in order to conduct the step (b), since the force concentrates on the vicinity of the top roller disposed in the tin bath 3.

[0012] In the gas mixture of the above-mentioned step (a), it is preferable that the vapor of the organic titanium compound has a partial pressure of from 0.1 to 10 kPa, more preferably from 1 to 5 kPa, and that the oxygen gas has a partial pressure of from 3 to 40 kPa, more preferably from 10 to 36 kPa. With this, it becomes possible to obtain an anatase-type titanium oxide film that is superior in photocatalytic activity and strength. It is preferable to make the partial pressure of the oxygen gas higher in the preferable range, in order to provide the gas mixture with an oxidative atmosphere. With this, it becomes possible to produce the titanium oxide more effectively. If the oxygen concentration of the gas mixture is too high, the gas mixture may become inflammable to increase the fire risk. The steam contained in the gas mixture may accelerate the polycondensation of the organic titanium compound. This may interfere with pyrolysis of the organic titanium compound. Furthermore, scales may occur by the presence of the steam, during the introduction of the gas mixture into the nozzle for discharging the gas mixture. Thus, the partial pressure of the steam contained in the gas mixture is preferably not higher than 0.1 kPa, more preferably not higher than 0.01 kPa. In fact, it is the most preferable that the gas mixture does not contain steam.

[0013] Even if the temperature of the glass substrate is lower than 300°C, it is possible to form the outermost titanium oxide layer on the glass substrate. In this case, however, adhesion of the outermost layer to the glass substrate may become insufficient. Still furthermore, the X-ray diffraction chart of the obtained titanium oxide may not have clear peaks, and thus the titanium oxide may become insufficient in photocatalytic activity. Thus, the outermost titanium oxide layer is formed on a glass substrate heated preferably at a temperature of at least 300°C, more preferably at least 350°C, still more preferably 400-600°C. In particular, if the outermost layer of an anatase-type titanium oxide is formed on a glass substrate of at least 500°C, the outermost layer becomes substantially high in photocatalytic activity. In this case, if the thickness of the outermost layer, which is directly formed on a soda-lime glass substrate, is at least 50nm, it becomes possible to maintain the photocatalytic activity of the titanium oxide. In other words, alkali components, particularly sodium ions, do not interfere with the photocatalytic activity of the titanium oxide, and thus it is not necessary to provide an interlayer (barrier) between the glass substrate and the outermost layer. If the thickness of the outermost layer is greater than 300nm, the outermost layer becomes conspicuous in iridescence and thus may not be favorable in appearance.

[0014] As mentioned above, the titanium oxide of the invention is characterized in that an X-ray diffraction chart (pattern) of the titanium oxide has at least a first peak at a first spacing of 3.5 angstroms between adjacent crystallographic planes of the titanium oxide and a second peak at a second spacing of 1.9 angstroms between adjacent crystallographic planes of the titanium oxide and that the second peak has a height that is at least one-tenth of a height of the first peak (see Fig. 2). With this, the titanium oxide becomes substantially high in photocatalytic activity. The above-mentioned first and second spacings respectively correspond to diffraction angles 2 $\theta$  of 25 and 48 degrees, as shown in Fig. 2. Furthermore, it is preferable that an X-ray diffraction chart of the titanium oxide has a third peak at a third spacing of 1.7 angstroms (2 $\theta$  : 55 degrees) and a fourth peak at a fourth spacing of 1.5 angstroms (2 $\theta$  : 63 degrees), as shown by the X-ray diffraction pattern [A] of Fig. 2. As mentioned above, the second peak has a height that is at least one-tenth of the height of the first peak. We assume that this means a good balance between the first peak in a direction of Miller indices 101 and the second peak in a direction of Miller indices 200 to make the titanium oxide high in photo-

catalytic activity.

[0015] In the invention, it is optional to provide at least one first interlayer having an intermediate refractive index of 1.55-2.0 and/or at least one second interlayer having a high refractive index of 2.6-2.9, between the glass substrate and the outermost titanium oxide layer. In fact, the first and second interlayers may be laminated alternately. The first interlayer is made of for example, aluminum oxide, tin oxide, indium oxide, zinc oxide or silicon oxycarbide, and the second interlayer contains as a main component thereof at least one metal oxide selected from chromium oxides, iron oxides, cobalt oxides and copper oxides. It is preferable to adjust the refractive index and thickness of the first or second interlayer such that the reflectance and excitation purity of the outermost layer are lowered by the interference of the reflected light from the first or second interlayer.

[0016] In the invention, it is optional that the at least one layer, having the outermost titanium oxide layer, is formed on one major surface of the glass substrate, and a reflective metal layer is formed on the other major surface of the glass substrate. With this, the obtained glass pane can be used as an antifogging mirror.

[0017] The following nonlimitative examples are illustrative of the present invention.

#### EXAMPLE 1

[0018] An outermost titanium oxide layer was directly formed on a glass substrate 2 by using a float glass production line 1 of Fig. 1, as follows. The glass substrate 2, having a thickness of 3 mm and a width of 3.6 m, was allowed to flow continuously at a speed of 8 m per minute in the production line 1. A nozzle 5, made of stainless steel, for forming the outermost layer on the glass substrate 2 was disposed 1.5 m downstream from an exit partition wall 8 of a tin bath 3. In fact, the nozzle 5 was disposed, at a height of 15 mm above the glass substrate 2, in the inside of an annealing chamber 4 and in the vicinity of the entrance of an annealing chamber 4, as illustrated. At the position of the nozzle 5, the temperature of the glass substrate's surface was found to be 570-580°C by the measurement with a radiation thermometer. The temperature of the bottom surface of the nozzle 5 was adjusted to be in a range of 200-220°C by allowing a heat carrying oil of 180°C to flow continuously through the interior of the nozzle 5. As shown in Fig. 1, the nozzle 5 was symmetrical about an axis of symmetry that is perpendicular to the direction of the flow of the glass substrate 2 in the production line 1. In fact, the nozzle 5 had a discharge slit 6 for discharging the gas mixture at a middle portion of the nozzle 5, and exhaust slits 7 for exhausting the gas mixture at both sides of the discharge slit 6. Each of the discharge and exhaust slits 6, 7 extends 3.2 m in a direction perpendicular to the direction of the flow of the glass substrate 2. The distance between the exhaust slits 7, 7 in the direction of the flow of the glass substrate 2 was 600 mm. A region between the exhaust slits 7, 7 was provided for forming the outermost layer on the glass substrate 2.

[0019] Separately, the gas mixture was prepared, as follows. At first, titanium tetraisopropoxide, preliminarily heated at 100°C, was atomized or sprayed at a rate of 240 g per minute into a hermetic stainless-steel container of a double wall structure, while a nitrogen gas, preliminarily heated at 180°C, was introduced as a carrier or atomizing gas into the container at a rate of 200 nL per minute. Then, the titanium tetraisopropoxide in the container was totally turned into a vapor by heat of the container having a double wall's void space filled with a heat carrying oil of 180°C. A mixture of titanium tetraisopropoxide (gas) and nitrogen gas was allowed to flow through a pipe from the container and then was mixed with an air preliminarily heated at 180°C and having a flow rate of 300nL per minute. The resultant gas mixture was lead to the discharge slit 6, while it was maintained at 180°C. Then, the resultant gas mixture was blown upon the glass substrate 2 from the discharge slit 6, thereby to form a titanium oxide film on the glass substrate 2 by pyrolysis under normal pressure. Each of the nitrogen and air of the resultant gas mixture was -60°C in dew point. The calculated partial pressures of the oxygen, titanium compound, and steam were about 12kPa, about 4kPa and 0.001kPa, respectively. The refractive index and thickness of the titanium oxide film were respectively found to be 2.38 and 135nm, from the results of the spectral reflectance of the titanium oxide film. The titanium oxide film was subjected to all X-ray diffraction analysis with CuK $\alpha$  X-rays produced by an output voltage of 50kV and an electric current of 200mA, incident angles starting from 2 degrees, a scanning speed of 5 degrees per minute, a diverging slit angle of 1/2 degrees, and a scattering slit angle of 1/2 degrees. The result of the X-ray diffraction analysis is shown by an X-ray diffraction pattern [A] of Fig. 2. This pattern was found to have first, second, third and fourth peaks at spacings between adjacent crystallographic planes of the titanium oxide of 3.5, 1.9, 1.7 and 1.5 angstroms. These spacings correspond to diffraction angles 2 $\theta$  of 25, 48, 55 and 63 degrees respectively, as shown in Fig. 2. The relative heights of the first, second, third and fourth peaks were respectively 8, 2, 1 and 1, as shown in Fig. 2. In comparison with the X-ray diffraction pattern of Fig. 3 of Referential Example, in which a commercial anatase-type titanium oxide powder was bonded to a glass holder by a bonding agent (i.e., starch), it is assumed that the first, second, third and fourth peaks of the X-ray diffraction pattern [A] of Fig. 2 are diffraction lines generated by the titanium oxide's adjacent crystallographic planes 101, 200, 211 and 204, respectively. In fact, each numeral of three figures in parenthesis of Fig. 3 is Miller indices. The titanium oxide film of Referential Example had a white color and thus was not transparent. Furthermore, the titanium oxide powder of Referential Example comes off easily, and thus the titanium oxide film of Referential Example is substantially different from that of the invention.

[0020] In Example 1, the obtained glass pane having the titanium oxide film formed on the glass substrate was subjected to an abrasion resistance test. In this test, the titanium oxide film was abraded 200 times by a Taber abraser defined in Japanese Industrial Standard (JIS) R 3212. The transmittance after the abrasion resistance test was about 3.2% higher than that before this test. This means that the titanium oxide film was bonded to the glass substrate with a high bonding strength.

[0021] The photocatalytic activity of the obtained glass pane having widths of 100mm was determined as follows. At first, the glass pane was immersed in an oleic acid solution, and then withdrawn therefrom at a speed of 1.2mm per second. After that, water was dropped onto the titanium oxide film, and then the contact angle of water drop thereon was measured. The result of this was about 30 degrees. Then, the titanium oxide film was irradiated for 3 hr with ultraviolet rays using an ultraviolet lamp having an intensity of 0.5mW/cm<sup>2</sup>. Then, the contact angle of water drop was measured again, and the result was 8 degrees. This means that oleic acid was decomposed during the ultraviolet irradiation, and thus the titanium oxide film's surface became hydrophilic.

[0022] The obtained glass pane had a reflectance from the titanium oxide film of 35%, a dominant wavelength of 440nm, an excitation purity of 21%, and a transmittance of 62%.

[0023] The calculated rate for forming the titanium oxide film is as follows:

$$(\text{Film Thickness } 135\text{nm}) \times (\text{Glass Substrate Moving Speed } 8\text{m/min.}) \div (\text{Film Width } 600\text{mm}) = 1.8 \mu\text{m/min.}$$

[0024] The calculated efficiency for forming the titanium oxide film is as follows:

$$\begin{aligned} & (\text{Film Thickness } 135\text{nm}) \times (\text{Film Area } 3.2\text{m} \times 8\text{m})/\text{min.} \\ & \times (\text{TiO}_2 \text{ Density } 3.84) \div 1,000 \div (\text{TiO}_2 \text{ Molecular Weight } 80) \\ & \div (\text{Ti Alkoxide Supply Rate } 240\text{g/min}) \div (\text{Ti alkoxide Molecular Weight } 284) = 19.6\%. \end{aligned}$$

#### EXAMPLE 2

[0025] In this example, Example 1 was repeated except in that the supply rate of titanium tetraisopropoxide was 100 g/min in place of 240 g/min and that the position of the nozzle 5 was 40m downstream from the exit partition wall 8 of the tin bath 3. The temperature of the glass substrate 2 at the position of the nozzle 5 was in a range of 390-400°C. The calculated partial pressures of the titanium compound, oxygen and steam of the gas mixture were 1.3kPa, 12kPa and 0.001kPa, respectively. The obtained titanium oxide film formed on the glass substrate was found to have a refractive index of 2.35 and a thickness of 45 nm. The obtained glass pane was found to have a visible light reflectance from the coated side of 30%, a dominant wavelength of 440nm, and an excitation purity of 15%. The result of the X-ray diffraction analysis is shown by an X-ray diffraction pattern [B] of Fig. 2. This pattern was found to have first and second peaks at spacings between adjacent crystallographic planes of the titanium oxide of 3.5 and 1.9 angstroms where the diffraction angles  $\theta$  are respectively 25 and 48 degrees. The relative heights of the first and second peaks were respectively 10 and 3, as shown in Fig. 2. The calculated rate and efficiency for forming the titanium oxide film on the glass substrate were 0.6  $\mu\text{m/min}$  and 15.7%, respectively. The glass pane was subjected to the same photocatalytic activity test as that of Example 1, except in that the ultraviolet irradiation time was 10hr. After this test, the contact angle of water drop was found to be 16 degrees.

#### EXAMPLE 3

[0026] In this example, a float glass production line 1 of Example 1 was used except in that another nozzle, which is similar to the nozzle 5 in construction, was disposed in the vicinity of the nozzle 5 such that the another nozzle was interposed between the nozzle 5 and the tin bath 3. The another nozzle was used for forming an aluminum oxide inter-layer on a glass substrate. In fact, aluminum acetylacetonato, NACEM aluminum of Nippon Chemical Industrial Co., Ltd., was transported through an stainless steel pipe having an internal diameter of 6mm, at a rate of 280 g/min by a device for quantitatively supplying powder, together with an air at a rate of 700L/min. This stainless steel pipe had a coiled portion of 12 m immersed in a heat carrying oil bath of 220°C. After passing through the coiled portion, the aluminum acetylacetonato turned into a vapor. The thus obtained mixture of the aluminum acetylacetonato and the air was blown upon the glass substrate from a discharge slit of the another nozzle, thereby to form an aluminum oxide film on the glass substrate. This film was confirmed to be an aluminum oxide film having a thickness of about 70nm by Auger electron spectroscopy, although X-ray diffraction lines of this film were not found. The aluminum oxide film was found to have a reflectance from the coated side of 9.5%, a refractive index of 1.61, and a thickness of 67nm.

[0027] Then, a titanium oxide film was formed on the aluminum oxide film in the same manner as that of Example 2

by using the nozzle 5 adjacent to the another nozzle. The obtained glass pane was found to have a visible light reflectance from the coated side of 14%, a dominant wavelength of 500nm, and an excitation purity of 3.5%. Thus, the reflected light from the coated side became more neutral as compared with those of Examples 1-2 by the provision of the aluminum oxide interlayer having an intermediate refractive index. The result of the X-ray diffraction analysis of the titanium oxide film was almost the same as that of Example 2. The glass pane was subjected to a photocatalytic activity test that is similar to that of Example 1. In fact, the ultraviolet irradiation times were 3 hr and 10 hr. After 3 hr, the contact angle of water drop was found to be 3 degrees. After 10 hr, it was found to be 1 degree.

#### EXAMPLE 4

[0028] In this example, Example 1 was repeated except in that the air preliminarily having a flow rate of 300nL per minute was replaced with a mixture of an air and an oxygen each having a flow rate of 150 nL/min. The calculated partial pressures of the oxygen, titanium compound and steam of the gas mixture were about 36kPa, about 4kPa and about 0.001kPa, respectively.

[0029] The titanium oxide film was found to have a refractive index of 2.38 and a thickness of 140nm, based on the spectral reflectance of the coated side of the glass pane. The X-ray diffraction pattern of the titanium oxide film was found to have first, second, third and fourth peaks at spacings between adjacent crystallographic planes of the titanium oxide of 3.5, 1.9, 1.6 and 1.4 angstroms where the diffraction angles  $2\theta$  are respectively 25, 48, 55 and 63 degrees. The relative heights of the first, second, third and fourth peaks were respectively 8, 3, 1 and 1. The result of the abrasion resistance test, the increase in transmittance, was about 3.0%. The photocatalytic activity test was conducted in the same manner as that of Example 2. After 10hr of this test, the contact angle of water drop was 3 degrees. The obtained glass pane was found to have a visible light reflectance from the coated side of 35%, a dominant wavelength of 440nm, an excitation purity of 21%, and a transmittance of 62%.

#### EXAMPLE 5

[0030] In this example, Example 1 was repeated except in that the supply rate of titanium tetraisopropoxide was 40 g/min in place of 240 g/min and that the mixture of titanium tetraisopropoxide (gas) and nitrogen gas was mixed with a nitrogen gas having a dew point of -30°C and a flow rate of 1,000nL/min, together with the air having a flow rate of 300 nL/min. The calculated partial pressures of the titanium compound, oxygen, and steam of the gas mixture were about 0.25kPa, 4kPa and 0.04kPa, respectively.

[0031] The titanium oxide film was found to have a refractive index of 2.37 and a thickness of 20nm, based on the spectral reflectance of the coated side of the glass pane. The obtained glass pane was found to have a visible light reflectance from the coated side of 18%, a dominant wavelength of 430nm, and an excitation purity of 19%. The X-ray diffraction pattern of the titanium oxide film was found to have first and second peaks at spacings between adjacent crystallographic planes of the titanium oxide of 3.5 and 1.9 angstroms where the diffraction angles  $2\theta$  are respectively 25 and 48 degrees. The relative heights of the first and second peaks were respectively 9 and 1. The result of the abrasion resistance test, the increase in transmittance, was about 3.0%. The rates and efficiency for forming the titanium oxide film on the glass substrate were 0.27  $\mu\text{m}/\text{min}$  and 17.4%, respectively. The photocatalytic activity test was conducted in the same manner as that of Example 2. After 10hr of this test, the contact angle of water drop was 10 degrees.

#### COMPARATIVE EXAMPLE 1

[0032] In this example, Example 2 was repeated except in that the position of the nozzle 5 was 70m downstream from the exit partition wall 8 of the tin bath 3 and that the amount of steam in the gas mixture was adjusted to have a partial pressure of 0.5kPa. The temperature of the glass substrate surface at the position of the nozzle was 260°C. The titanium oxide film was found to have a refractive index of 2.28 and a thickness of 20nm, based on the spectral reflectance of the coated side of the glass pane. In the abrasion resistance test, the titanium oxide film exfoliated from the glass substrate by 40 rotations of the Taber abraser. The result of the X-ray diffraction analysis of the titanium oxide film is shown by the X-ray diffraction pattern [C] of Fig. 2. In fact, the X-ray diffraction pattern was found to have only one peak at a spacing between adjacent crystallographic planes of the titanium oxide of 3.5 angstroms where the diffraction angle  $2\theta$  is 25 degrees. The photocatalytic activity test was conducted in the same manner as that of Example 2. After 10hr of this test, the contact angle of water drop was 31 degrees. It is assumed that the titanium oxide film was insufficient in compactness and too low in refractive index, since the glass substrate surface temperature was too low. Furthermore, it was found that the titanium oxide film was insufficient in crystallinity and thus in photocatalytic activity. It should be noted that scales of titanium oxide and titanium hydroxide accumulated on the device for forming the titanium oxide film and thus 30 minutes after the start of the CVD of the titanium oxide many streaks occurred on the titanium oxide film in a direction along the movement of the glass substrate.

## COMPARATIVE EXAMPLE 2

[0033] In this example, Example 1 was repeated except in that the titanium tetraisopropoxide was replaced with titanium tetrathoxide and that the supply rates of the titanium tetrathoxide and the air were 300g/min and 20nL/min, in place of 240g/min and 300nL/min, respectively. The partial pressures of the oxygen, titanium compound and steam of the gas mixture were 1.8kPa, 13kPa and 0.001kPa, respectively. The titanium oxide film was found to have a refractive index of 2.51 and a thickness of 42nm, based on the spectral reflectance of the coated side of the glass pane. The photocatalytic activity test was conducted in the same manner as that of Example 2. After 10hr of this test, the contact angle of water drop was 29 degrees. It is assumed that the titanium oxide film was insufficient in crystallinity and photocatalytic activity, since the partial pressure of the titanium compound vapor was too high and the partial pressure of the oxygen was too low. Making a comparison between the results of Examples 1-5 and the results of Comparative Example 2, titanium ethoxide may be inferior to titanium isopropoxide in obtaining of photocatalytic activity.

## COMPARATIVE EXAMPLE 3

[0034] In this comparative example, Example 1 was repeated except in that a methylene chloride solution containing 20 wt% of titanium diisopropoxybisacetylacetonato, T-50 (trade name) of Nippon Soda Co., Ltd., was sprayed onto the glass substrate at a rate of 2,500 g/min, thereby to form a titanium oxide film on the glass substrate by pyrolysis. In fact, the methylene chloride solution was sprayed from a spraying device under a liquid pressure of 90 kg/cm<sup>2</sup> at a level 250mm higher than the glass substrate surface, while a nozzle of the spraying device was reciprocated at a speed of 2 m/s, in a direction perpendicular to that of the movement of the glass substrate, with an amplitude of 2.5 m. Furthermore, a space for conducting the spraying was enclosed by a chamber, and the atmosphere of the chamber was exhausted at a rate of 15,000 nm<sup>3</sup> per hour.

[0035] The obtained titanium oxide film was found to have a refractive index of 2.29 and a thickness of 42nm, based on the spectral reflectance of the coated side of the glass pane. The X-ray diffraction pattern of the titanium oxide film was found to have only first and second peaks at spacings between adjacent crystallographic planes of the titanium oxide of 3.5 angstroms and 1.9 angstroms where the diffraction angles  $2\theta$  are 25 and 48 degrees, respectively. The height of the second peak was one-twelfth of that of the first peak. The glass pane was subjected to the abrasion resistance test. In this test, the increase of transmittance after 200 rotations of the Taber abramer was 6.6%. This means that the titanium oxide film was insufficient in adhesion strength. The glass pane did not have a high photocatalytic activity as those of Examples 1-5. Thus, it is assumed that the titanium oxide film of Comparative Example 3 is substantially lower in crystallinity than those of Examples 1-5.

[0036] The entire disclosure of Japanese Patent Application No. 9-233689 filed on August 29, 1997, including specification, claims, drawings and summary, is incorporated herein by reference in its entirety.

## Claims

## 1. A photocatalytic glass pane comprising:

a glass substrate; and  
at least one layer formed on at least one major surface of said glass substrate, said at least one layer having an outermost layer made of a photocatalytic titanium oxide, said outermost layer being prepared by a chemical vapor deposition,  
wherein said titanium oxide is such that an X-ray diffraction chart of said titanium oxide has at least a first peak when a spacing between adjacent crystallographic planes of said titanium oxide is 3.5 angstroms and a second peak when a spacing between adjacent crystallographic planes of said titanium oxide is 1.9 angstroms and that said second peak has a height that is at least one-tenth of a height of said first peak.

2. A glass pane according to claim 1, wherein said X-ray diffraction chart of said titanium oxide further has a third peak when a spacing between adjacent crystallographic planes of said titanium oxide is 1.7 angstroms and a fourth peak when a spacing between adjacent crystallographic planes of said titanium oxide is 1.5 angstroms.

3. A glass pane according to claim 1, wherein said X-ray diffraction chart of said titanium oxide is obtained by allowing K $\alpha$  X-rays from a copper target to impinge against said outermost layer.

4. A glass pane according to claim 1, wherein said titanium oxide is of an anatase type.

5. A glass pane according to claim 1, wherein said outermost layer has a thickness that is not greater than 300 nm.

6. A glass pane according to claim 1, wherein said at least one layer further has an interlayer interposed between said glass substrate and said outermost layer, said interlayer having a refractive index of from 2.6 to 2.9 and comprising at least one metal oxide selected from the group consisting of chromium oxides, iron oxides, cobalt oxides and copper oxides.
7. A glass pane according to claim 1, wherein said at least one layer further has an interlayer interposed between said glass substrate and said outermost layer, said interlayer having a refractive index of from 1.55 to 2.0 and comprising at least one compound selected from the group consisting of aluminum oxides, tin oxides, indium oxides, zinc oxides and silicon oxycarbide.
8. A glass pane according to claim 1, wherein said chemical vapor deposition is conducted by a method comprising the sequential steps of:
  - (a) providing a gas mixture comprising a vapor of an organic titanium compound and an oxygen gas; and
  - (b) bringing said gas mixture into contact with said glass substrate that is under a heated condition, thereby to form said outermost layer on said glass substrate.
9. A glass pane according to claim 8, wherein said gas mixture further comprises a nitrogen gas.
10. A glass pane according to claim 9, wherein said vapor of said organic titanium compound has a partial pressure of from 0.1 to 10 kPa, and said oxygen gas has a partial pressure of from 3 to 40 kPa.
11. A glass pane according to claim 8, wherein said gas mixture is free of a steam.
12. A glass pane according to claim 1, wherein said at least one layer is formed on one major surface of said glass substrate, and a reflective metal layer is formed on the other major surface of said glass substrate, so that said glass pane is usable as an antireflective mirror.
13. A method for producing a photocatalytic glass pane, said photocatalytic glass pane comprising a glass substrate; and at least one layer formed on at least one major surface of said glass substrate, said at least one layer having an outermost layer made of a photocatalytic titanium oxide, said outermost layer being prepared by a chemical vapor deposition, wherein said titanium oxide is such that an X-ray diffraction chart of said titanium oxide has at least a first peak when a spacing between adjacent crystallographic planes of said titanium oxide is 3.5 angstroms and a second peak when a spacing between adjacent crystallographic planes of said titanium oxide is 1.9 angstroms and that said second peak has a height that is at least one-tenth of a height of said first peak, said method comprising the sequential steps of:
  - (a) providing a gas mixture comprising a vapor of an organic titanium compound and an oxygen gas; and
  - (b) bringing said gas mixture into contact with said glass substrate that is under a heated condition, thereby to form said outermost layer on said glass substrate.
14. A method according to claim 13, wherein said gas mixture further comprises a nitrogen gas.
15. A method according to claim 13, wherein said vapor of said organic titanium compound has a first partial pressure of from 0.1 to 10 kPa, and said oxygen gas has a second partial pressure of from 3 to 40 kPa.
16. A method according to claim 15, wherein said first partial pressure is from 1 to 5 kPa, and said second partial pressure is from 10 to 36 kPa.
17. A method according to claim 13, wherein said gas mixture is free of a steam.
18. A method according to claim 13, wherein the step (b) is conducted at a temperature not higher than 750°C.
19. A method according to claim 13, wherein said glass substrate is heated at a temperature not lower than 300°C.
20. A method according to claim 19, wherein said temperature of said glass substrate is from 400 to 600°C.
21. A method according to claim 20, wherein said temperature of said glass substrate is from 500 to 600°C.



22. A method according to claim 13, wherein, prior to the step (b), an interlayer is formed on said glass substrate, said interlayer having a refractive index of 2.6-2.9 and comprising at least one metal oxide selected from the group consisting of chromium oxides, iron oxides, cobalt oxides and copper oxides.
23. A method according to claim 13, wherein, prior to the step (b), an interlayer is formed on said glass substrate, said interlayer having a refractive index of from 1.55 to 2.0 and comprising at least one metal oxide selected from the group consisting of aluminum oxides, tin oxides, indium oxides, and zinc oxides.
24. A method according to claim 13, wherein, prior to the step (b), an interlayer is formed on said glass substrate, said interlayer having a refractive index of from 1.55 to 2.0 and comprising silicon oxycarbide.
25. A method according to claim 13, wherein said organic titanium compound is a titanium alkoxide.
26. A method according to claim 25, wherein said titanium alkoxide is at least one selected from the group consisting of titanium tetraisopropoxide, titanium tetramethoxide, titanium tetraethoxide, and titanium monochlorotrialkoxide.
27. A method according to claim 22, wherein said interlayer is formed by bringing a gas mixture into contact with said glass substrate, said gas mixture comprising a vapor of at least one compound of at least one metal selected from the group consisting of chromium, iron, cobalt and copper.
28. A method according to claim 27, wherein said at least one compound is at least one acetylacetonato of said at least one metal.
29. A method according to claim 23, wherein said interlayer is formed by bringing a gas mixture into contact with said glass substrate, said gas mixture comprising a vapor of at least one compound of at least one metal selected from the group consisting of aluminum, tin, indium and zinc.
30. A method according to claim 29, wherein said at least one compound is at least one acetylacetonato of said at least one metal.
31. A method according to claim 24, said interlayer is formed by bringing a gas mixture into contact with said glass substrate, said gas mixture comprising silane gas, an ethylenic hydrocarbon gas and carbon dioxide.

FIG. 1

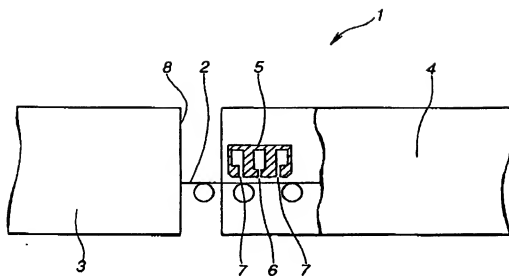


FIG.2

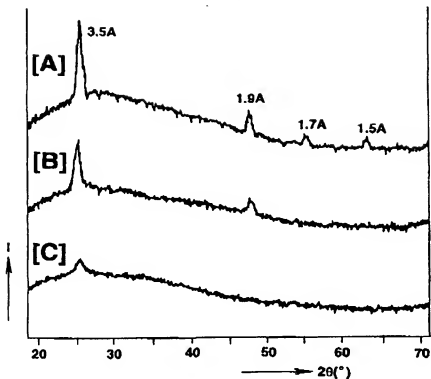
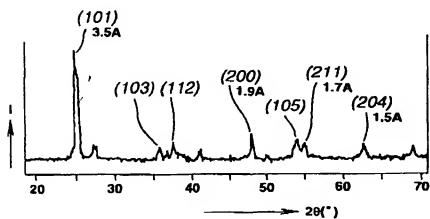


FIG.3



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<b>(57) Abstract</b>		
A self-cleaning glass, usable, for example, as a window or windshield, coated with an optically clear and abrasion resistant film comprising a photocatalyst is formed on common glass by depleting alkali metal oxides from the glass and/or by forming a barrier to the migration of such oxides from the glass into the photocatalyst-containing coating. Upon exposure to light absorbed by the photocatalyst and in the presence of air, the film strips grime and contaminants from the glass surface.		

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## SELF-CLEANING GLASS AND METHOD OF MAKING THEREOF

## Field of Invention

This invention relates to the photocatalytic oxidative stripping of organic  
5 contaminants from the surface of glass and the process of making such photocatalytic  
glass.

## Background of the Invention

It has been known for some time that photocatalysts, particularly titanium  
10 dioxide in the anatase phase, accelerate the air-oxidation of organic compounds upon  
exposure to light, usually ultraviolet, absorbed by the photocatalyst. See, for example,  
*Photocatalytic Purification of Water and Air*, D.F. Ollis and H. Al-Ekabi, eds.,  
Proceedings of the First International Conference on  $\text{TiO}_2$  Photocatalytic Purification and  
Treatment of Water and Air, London, Ontario, Canada, 1993, Elsevier, Amsterdam. The  
15 major sections of the book describe the theory and fundamentals of titanium dioxide  
( $\text{TiO}_2$ ) photocatalysis, photocatalyzed water and air treatment, reactor design and  
photocatalytic oxidation process economics. In all of these applications the photocatalyst  
is bound to a ceramic substrate to which it adheres. For example, on page 123, R. W.  
Mathews describes  $\text{TiO}_2$  coated glass mesh and  $\text{TiO}_2$  coated glass tube-based  
20 photoreactors. Another reactor with a  $\text{TiO}_2$  coated glass tube is described by T. Ibusuki et  
al. on page 376. The photocatalytic films described were all light scattering, as they were  
made of photocatalysts such as Degussa P25, e.g., with an abundance of titanium dioxide  
particles approximately 0.1-0.3 microns in diameter. This particle size, even in the  
thinnest films, produces a milky appearance. Such light scattering films are not efficient  
25 or useful in applications such as clear, self-cleaning glass surfaces for windows and  
mirrors.

It is also known that clear and adherent, non-light scattering  $\text{TiO}_2$  films can  
be made. Such known films are applied to optical lenses of optical instruments to provide  
scratch resistance and are also applied in anti-reflective optical coatings, usually by  
30 reactive evaporation or by reactive sputtering of titanium in an oxygen-containing  
atmosphere. Such coatings can also be made by applying a solution containing a  
precursor of a photocatalyst, e.g.,  $\text{TiO}_2$ , to a glass surface, forming a precursor film and

heating to a high temperature where organic matter in the precursor film is oxidized and  $\text{TiO}_2$  is crystallized. However, on substrates consisting of glasses comprising more than about 10% by weight of combined alkali metal oxides, particularly sodium oxide ( $\text{Na}_2\text{O}$ ) and potassium oxide ( $\text{K}_2\text{O}$ ), these films are poor photocatalysts, i.e., when exposed to sunlight in air they do not oxidize organic contaminants at a rate adequate to maintain a clean glass surface. For example, when coated with a film of stearic acid, they oxidize it under  $2.4 \text{ mWcm}^{-2}$  365 nm irradiance at a rate of 4nm per hour or less, i.e., reduce the thickness of the stearic acid film by less than 4nm per hour. Under the same conditions, a good photocatalyst strips a film of stearic acid at a rate of about 20nm per hour or more, i.e., reduces the thickness of the stearic acid film by about 20 nm per hour (or more).

It has now been found that migration of sodium into the photocatalytic film, (e.g., leaching out of common soda lime glass), particularly during the formation of the film from precursors, results in severely reduced activity of the photocatalytic films and reduced photocatalytic efficiency of self-cleaning glass. It would be highly advantageous to provide a means for reducing the deleterious effects of migrating alkali metal oxides and/or sodium on the photoactivity of self-cleaning, photocatalytic film-coated glasses.

#### Summary of the Invention

We have discovered a barrier to the migration of alkali metal oxides from a glass substrate into the photocatalytic coating that is thin, yet effective. This barrier layer slows or blocks the migration of alkali metal oxides into the photocatalyst layer during its formation from a precursor and also after its formation from the precursor.

The preferred barrier is formed by first introducing into the near surface region of the glass to be coated, protons, i.e. hydrogen ions, by exchanging alkali metal ions with protons of an acid and/or by hydrolytic cleavage of silicon-oxygen-silicon bonds with an acid, in a process called "acid etching" or simply "etching". The hydrogen or proton-containing glass layer is then reacted with a precursor of an oxide of a four-valent element, preferably a precursor of crystalline titania or zirconia comprising inorganic oxide. In this process, a thin, sodium-migration blocking layer comprising titanium, silicon and oxygen and/or zirconium, silicon and oxygen is formed.

A sodium migration blocking layer is also formed when the proton or hydrogen-containing glass (acid glass), is reacted with a precursor of silica. A preferred process of forming the acid glass layer includes etching with acid, most preferably boiling in 9 M sulfuric acid. The sodium migration reducing barrier layer is preferably formed upon heating the acid glass with a precursor of titania, and/or zirconia to a temperature in excess of about 300°C and less than about 500°C and preferably about 400°C.

The photocatalytic activity of a formed, optically clear  $\text{TiO}_2$  layer on glass is also enhanced by treating the  $\text{TiO}_2$  coated glass with a material that reacts with sodium oxide, particularly with a dilute acid that does not dissolve  $\text{TiO}_2$  in the form in which it is included in the coating. In general, the anion of an acid that does not dissolve  $\text{TiO}_2$  does not form a strong complex with four valent titanium. These types of acids include protic acid, Lewis acid and Bronsted acid, and can be in liquid or gas form. For example, nitric, perchloric, and tetrafluoroboric acids are useable in the invention, as they are not known to form complexes with four valent titanium. Chlorides, fluorides and sulfates are generally not useable in the invention because they are known to strongly complex with titanium (IV).

The imposition of a sodium migration blocking layer on the surface of a sodium containing glass, e.g., common soda lime glass, assures formation of the desired photocatalytic anatase phase by prohibiting migration of sodium from the glass and into the precursor of the photocatalytic film. This barrier also reduces sodium contamination of the anatase phase that lowers the photocatalytic activity. A particularly useful sodium migration blocking layer is formed by applying a film of an organotitanate that decomposes upon heating in air, a nascent, yet non-crystalline precursor of anatase  $\text{TiO}_2$ , and reacting the precursor with the sodium-depleted acid glass prior to final calcining of the coated glass and at an elevated temperature, preferably about 450°C. After final calcination, a transparent, non-scattering, adherent nanocrystalline photocatalytic oxide film is produced, with a distinct, sodium migration-blocking interface between the glass and the photocatalytic film.

The photocatalyst coated glass of the invention, when exposed to ultraviolet light, efficiently cleans itself of organic contaminants. This photocatalyst coated glass of the invention is particularly useful in applications such as photocatalytically self-cleaning windows, windshields and mirrors.



### Brief Description of the Figures

Figure 1 is a graph showing the UV absorption spectra of  $\text{TiO}_2$  films on fused silica.

Figure 2 is FTIR spectra of stearic acid coated on clear  $\text{TiO}_2$  film on fused silica prior to (dotted line) and after (solid line) exposure to UVA light for 7.5 minutes.

Figure 3 is a graph showing the UV absorption spectra of  $\text{TiO}_2$  films on etched (dashed line) and on non-etched soda lime glass (solid line).

Figure 4 is a graph showing the effect of the calcination temperature on UVA, i.e., near UV, photoactivity of clear films of titanium dioxide: (A) Two layers of  $\text{TiO}_2$  on fused silica, (B) Two layers of  $\text{TiO}_2$  on etched glass, (C) One layer of  $\text{TiO}_2$  on etched glass, (D) One layer of  $\text{TiO}_2$  on one layer of  $\text{ZrO}_2$  on etched glass.

Figure 5 is a graph showing the effect of etching duration on the photoefficiency of clear  $\text{TiO}_2$  films on soda lime glass.

### Detailed Description of the Preferred Embodiment

The invention is directed toward self-cleaning glass and methods of making the same. Photocatalytic films can form the basis for self-cleaning or photooxidatively cleaning glass, useful, for example, as self-cleaning windows, mirrors, optical components, eyeglass lenses, and automotive windshields. When using photocatalyst films, e.g.  $\text{TiO}_2$ , in these applications, the following should be optimized: the absence of scattering of visible light; abrasion resistance to an extent that the film is typically not damaged when cleaned or when impacted by dust particles; and an adequate photooxidation rate or efficiency in order to maintain a relatively clean glass surface. The coated self-cleaning glasses of the invention provide an abrasion resistant, photoefficient, optically clear, self-cleaning glass.

Deposition of organic contaminants on glass usually reduces visibility. Furthermore, light particularly from headlights of oncoming cars and from the sun when the sun is low on the horizon, interferes with driving when the windshield is contaminated. Films of organic contaminants smeared on the windshield by wipers operating in rain also add to the hazard of driving. Light scattered from contaminants on outside or inside rearview mirrors of cars impairs visibility in these mirrors. Dirt or fingerprints on lenses

or eyeglasses impair vision. The inventive films maintain surfaces clean of organic contaminants. Inorganic, non-oxidizable contaminants are readily removed by being blown or washed off, once the organic matter that makes them stick to the glass surface is oxidized.

5           The most preferred method for preparing photocatalytic glass is by acid etching the glass followed by application of the photocatalyst composition and then calcination.

### **Photocatalytic Film**

10           The photocatalytic film coated glasses of the invention, e.g. containing photocatalytic particles and adherent to glass, are optically clear. They may have a tint or color, but do not absorb or scatter visible light so as to impair visibility through the glass or cause severe glare. The photocatalytic films also adhere to glass and resist abrasion. An inventive film adhering to glass cannot be removed by pressing adhesive tape against  
15 it, as discussed below in Example 1, and rapidly pulling on it (Tape Test). An abrasion resistant film of the invention is not damaged when cleaned with wet or dry paper or cloth, and it typically is not scribed by a pencil of H2 hardness or softer. In general, the photocatalytic film is formed of photocatalytic particles, e.g., TiO<sub>2</sub>, cast onto acid glass and calcined for specific adherence to the glass.

20           The photocatalyst-containing films of the invention contain a material that, upon exposure to light, particularly UV light, accelerates the oxidation in air of organic compounds absorbed or deposited on the film. One example of such a film is a film containing crystalline, preferably anatase, titanium dioxide. The film is well bound to glass in the present invention, generally through an intermediate barrier layer that prevents  
25 migration of alkali metal oxides, e.g. sodium, yet is transparent to visible light.

### **Glass**

          The glasses useful in the present invention have varied compositions. The most commercially important and most common glasses comprise sodium and calcium  
30 ions and have a network formed of bonds of silicon and oxygen atoms.

          The self-cleaning glasses of this invention are usually photocatalytic films cast on common glass, which is formed of silicon dioxide, alkali metal oxides (oxides of

Column I metals of the periodic table), particularly sodium and potassium, and oxides of alkaline earth metals (oxides of Column 2 metals of the periodic table), particularly calcium. In general, the ratio of the number of oxygen atoms to the number of silicon atoms is between 2.2 and 2.7 in the glasses of the invention. In the preferred glasses, the ratio of oxygen atoms to silicon atoms is between 2.2 and 2.5. The glasses may contain other oxides, such as oxides of trivalent or tetravalent rare earths or oxides of aluminum, boron, antimony, germanium, lead and tin. The glasses are transparent, meaning that they can be seen through and are useful as windows, mirrors, windshields, and the like. An example of glass commonly used in such applications and useful in the invention is soda lime glass.

The method of the invention is intended to prevent migration of alkali metal oxides from glass, particularly of sodium and/or potassium, into the precursor of the photocatalytic film and/or into the photocatalyst film by creating a barrier to the migration. When excessive sodium migration is prevented, the photocatalytic film formed upon calcining of its precursor, can efficiently clean its surface of oxidizable contaminants such as carbon-rich organic films.

Glass that is commercially used in windows, mirrors, and optical lenses typically contains significant amounts of alkali metal oxides, such as sodium oxide and potassium oxide (usually at least about 10% by weight). Thus, the methods and coated glasses of the present invention provide for the first time an economically feasible self-cleaning clear glass.

### **Photocatalyst**

Photocatalysts useful in this invention are generally photoconductors or semiconductors having band gaps greater than 2.5eV and smaller than 4.5eV. The photocatalytic films are generally less than one micron thick, preferably about 40-80 nm thick, and consist of sufficiently small particles to avoid scattering of visible light. Alternatively, the crystallites of the photocatalytic particles are densely packed and oriented so that they do not scatter visible light. The preferred photocatalysts are crystalline oxides, particularly crystalline oxides comprising titanium, tin, tungsten or molybdenum. A particularly useful photocatalyst is titanium dioxide in the anatase phase. Other photocatalysts include  $\text{TiO}_2$  with co-catalysts such as Pt, Pd, Au, Ag, Cu, W, Mo, or

their sulfides and oxides; compound oxides such as  $(\text{SrTiO}_3)$  or  $\text{CaTiO}_3$ , and  $\text{TiO}_2$  in the rutile phase or in the mixed anatase and rutile phases. While a preferred photocatalyst, titanium dioxide, is exemplified herein, it is understood that other photocatalysts, e.g., those described above, forming clear films on glass may also be used.

5 Titanium dioxide in the anatase or the rutile phases has an index of refraction of visible (yellow) light greater than about 2.4. Coating of photocatalyst films on glass having a low refractive index, e.g., soda lime glass which has a refractive index below 1.6, causes an increase in the refractive index. In the specific case of automotive windshields such an increase can be undesirable, because as the angle between the  
10 dashboard and the windshield is reduced or the index of refraction of the windshield is raised, the reflected image of the dashboard becomes visible to the driver looking through the windshield. Such reflection is reduced by forming the photocatalytic film of a combination of the photocatalyst and a material having a lower refractive index than that of the photocatalyst. An example of such a film is one comprising non-crystalline silicon dioxide ( $\text{SiO}_2$ ) and anatase or rutile  $\text{TiO}_2$ . By way of example, if the film contains up to  
15 90 weight%  $\text{SiO}_2$ , then the index of refraction, in the visible, is only about 1.46. (As compared with 2.4-2.7 in the absence of  $\text{SiO}_2$ .)

#### **Photocatalyst Precursor**

20 In the present invention, a photocatalyst precursor is generally a film formed of a non-crystalline, three, four, or five-valent element, preferably of an oxide of such an element, which film forms an active photocatalytic film, eg., on calcining in air. The oxide is non-volatile at about  $600^\circ\text{C}$ , and the preferred three, four, or five-valent elements are titanium, tin, tungsten, or molybdenum. Most preferred is  $\text{Ti}^{4+}$ .

25 The photocatalyst-precursor films can be formed by their deposition from a liquid phase, or from a vapor phase. Useful photocatalytic precursor compositions include alkoxides, halides and oxyhalides of titanium, tin, tungsten, or molybdenum, e.g., a titanium tetralkoxide. A most preferred photocatalyst precursor is a film formed upon partial hydrolysis of titanium tetraalkoxide, followed by polymerization by condensation  
30 of the hydrolysate.

When a photocatalyst-comprising film having a lower refractive index than that of the photocatalyst itself is desired, for example for use in automotive windshields as

described above, the sol of which the photocatalysts precursor film is cast, in addition to the photocatalyst precursor, also contains a precursor of a lower refractive index film. For example, a preferred second component or precursor sol is a precursor of silicon dioxide, e.g., formed by co-hydrolyzing a silicon alkoxide, such as a silicon tetraalkoxide silicon, alkyltrialkoxide or dialkylalkoxide, co-dissolved with titanium alkoxide acetylacetonate. The ratio of the amounts of the silicon and titanium oxide precursors in the sol are adjusted as needed to obtain the desired refractive index. The photocatalytic film compositions range from pure titanium dioxide to compositions having a 1:10 titanium dioxide:silicon dioxide molar ratio. Preferred low-refractive index films comprise vitreous silicon dioxide and crystalline titanium dioxide phases.

#### **Barrier Layer**

In the present invention, a barrier layer is defined as a barrier that slows or stops the diffusion or migration of alkali metal ions (e.g., sodium ions) and/or alkali metal oxides (e.g., sodium oxide) into the photocatalyst precursor film or into the photocatalyst film. The barrier layer operates at the temperatures that the inventive photocatalyst precursor and photocatalyst films experience, and for the duration of the films.

In general, the barrier of the invention is the product of the reaction between hydrogen glass and a photocatalyst precursor as defined above. In the barrier, the most preferred three, four, or five-valent elements are  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Si}^{4+}$ . The most preferred barrier film is the reaction product between acid glass and the precursor of  $\text{TiO}_2$ , and includes the elements silicon, titanium, and oxygen.

#### **Forming Photocatalyst Coating on Glass**

A photocatalyst containing layer can be formed on the surface of the glass from a vapor phase or from a precursor dissolved or dispersed in a liquid. The preferred liquids containing the precursor are long lived sols. An example of these is described in Example 1. Stable sols can be formed, for example, of titanium tetraalkoxides, by reacting these first with acetylacetone, then with water. The sols contain polymers of the precursor species or crystallites of the photocatalyst that do not have a longest dimension greater than about 30nm and most preferably not greater than about 20 nm, and are preferably smaller than about 5nm in their larger dimension. The preferred liquid phase in which the

sol is dissolved or dispersed comprises alcohol in excess. Alcohols such as n-propanol, methanol, and butanol are useable.

A film of this liquid is applied to the glass surface, preferably to acid or etched glass, formed by acid etching (boiling in 9M sulfuric acid). The volume applied and the concentration of the precursor are selected so that the final thickness of the photocatalyst-containing layer will not be less than 10nm nor more than 500nm. The preferred final thickness is 20-200nm. The film can be formed by known methods, such as spraying microdroplets while the glass is cold or hot; dipping the glass in the liquid then removing it; pouring the liquid onto the glass and leveling the liquid layer mechanically or by spinning.

The film can also be formed by other methods, including a dry process, such as sputtering or evaporating a metal and then oxidizing it; or by reacting a low molecular weight molecular or metallic precursor in the gas phase prior to its deposition on the glass. For example, a titanium tetraalkoxide can be evaporated and decomposed either en route to or on the surface of the glass.  $\text{TiCl}_4$  can be reacted with water to form  $\text{TiO}_2$  en route to the surface. In addition, metallic Ti can be reactively sputtered in an  $\text{O}_2$  containing atmosphere to form a  $\text{TiO}_2$  film.

In contrast to prior attempts at coating common glass, relatively active photocatalytically self-cleaning films are formed on common window glass (soda lime glass) when the glass surface has been treated with a reactant that produces a hydrogen-containing acid glass by exchanging sodium ions with protons and/or by hydrolysis of Si-O-Si bonds, both of which may occur upon acid etching. When materials such as sodium oxide in the glass diffuse into part of the photocatalytic film layer near the glass, phases other than the desired crystalline photocatalyst phase form, and the desired crystalline phase can become excessively sodium-contaminated. As a result, some of the photoactivity of the film is lost. Reactants that are useful in exchanging sodium ions or other alkali metal ions of the glass at or near its surface (by protons) and thus increase the photocatalytic activity of the coated glass, are generally acids. When the acid glass reacts with a precursor of the crystalline  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or  $\text{SiO}_2$  film, a sodium migration reducing barrier layer is formed. Even in the presence of this barrier layer, some photoactivity of the crystalline titanium dioxide-comprising films on glass is still lost when sodium oxide

from the glass diffuses into part of the titanium dioxide layer near the glass. Photoactivity can be partially restored by subsequent acid treatment.

#### Acid Etching Glass-Pretreatment

5 Etching is the process whereby the reactive acid glass is formed.

Chemically, etching may involve one or both of the following processes: Exchange of alkali metal (e.g., sodium) ions of the glass with protons; and scission, through hydrolysis, of Si-O-Si bonds. In both processes, a glass having SiOH junctions is produced. An example of an etchant is boiling 9M aqueous sulfuric acid. This is the preferred etchant.

10 In a preferred process of making the photoactive film on glass, the glass is first exposed to acid so that sodium ions are extracted from its surface, being exchanged by protons and thereby forming an acid glass with silicon-bound OH-groups. The treatment with acid can be at ambient or, preferably, at higher temperatures, e.g., at the boiling temperatures of the acid. The glass surface can be rinsed following exposure to the acid with water, preferably deionized water, so as to remove any water soluble sodium salt. It has been noticed that treating of the glass with an acid prior to applying the photocatalytic coating to the glass leads to a higher photoefficiency. If the rinsing step is performed, the rinsing solution can be deionized water, or it can also contain a volatile base or ion such as ammonium hydroxide or an ammonium salt.

20 Preferred acids for etching glass include those which form a hydrogen glass upon reaction with the glass. An example of such an acid is 9M (50%) sulfuric acid. Most preferably, the glass is reacted with boiling 9M H<sub>2</sub>SO<sub>4</sub>.

The photocatalyst precursor or photocatalyst containing film is then deposited on the acid-treated surface. The acid treated glass should not be calcined prior to application of the catalytic film, as such calcining lowers the photocatalytic activity. It is suggested that reaction between the acid-treated glass and the photocatalyst crystalline precursor establishes a sodium-migration barrier at the interface of the glass and the film.

#### Photocatalyst Coating

30 The acid-treated and optionally rinsed glass is coated with the photocatalyst precursor. When coating is with a liquid, it is preferred that the precursor be in the form of a sol having an ambient temperature shelf life longer than a day. The sol

can be formed, for example, from a titanium tetraalkoxide, such as titanium tetraisopropoxide. The tetraalkoxide is first reacted in an alcohol solution, preferably in an excess alcohol, and preferably in an alcohol solution where the alcohol differs from the one that is evolved from the tetraalkoxide upon its hydrolysis. Although the sol can be formed by adding water to the titanium tetraalkoxide solution, in the preferred process the titanium tetraalkoxide is first reacted with a bifunctional  $Ti^{4+}$  complexing agent, such as acetylacetonate, to form a complex where the titanium to acetylacetonate ratio is 1:1. This complex is then hydrolyzed, preferably at room temperature, by adding water (preferably dissolved in alcohol), preferably at a molar ratio of 10 moles of water per 1 mole of titanium. The resulting precursor sol is generally stable, meaning that when stored for at least a day at a temperature between 5°C and 35°C the solution remains substantially clear.

A uniform film of the photocatalyst-containing compounds is cast on the glass through a process such as spinning, dipping, painting, spraying or applying an excess of solution then spreading it with a blade. The cast film is then allowed to dry.

### **Calcination**

The dried-film coated-glass is next calcined, e.g., heated at a temperature to form photocatalytic crystallites and cause the photocatalyst layer to adhere to the glass.

Calcination is preferably by heating in air at a rate resulting in a temperature increase of 50°C per minute, then holding at the desired calcining temperature, preferably for about 15 to 30 minutes. The coated glass is then cooled. At this point, this glass is photocatalytically self-cleaning within the scope of the invention.

The calcination temperature is generally in excess of 275°C and less than 650°C, and preferably is in the range of 400°C - 650°C. For calcining films on glass, the most preferred temperature is in the range of 400-550°C; for films on silica, the most preferred range is 550-600°C.

### **Acid Wash - Post Treatment**

The photocatalytic activity (i.e. the rate at which the glass cleans itself of an organic contaminant) of the already photocatalyst-coated glass can be further increased by a second treatment, termed "post-treatment", with acid. Post-treatment, even in the



absence of initial acid etching to form the acid glass, increases the low photocatalytic activity, though only to a lesser level than that observed when the glass was acid etched prior to deposition of the photocatalyst precursor. Applicants have found that multiple acid treatments can increase the self-cleaning glass's photoefficiency.

5 In this second, acid wash, post treatment step, the photocatalytic-film-coated glass is again exposed to an acid that reacts with or neutralizes sodium oxide or calcium oxide or a product of these. The preferred acids for this process step are strong mineral acids, the ions of which do not form strong complexes with four valent ions such as titanium ions ( $Ti^{4+}$ ). Dilute aqueous nitric acid, and particularly nitric acid of 0.1M to 10 3M concentration, with a preferred concentration of 0.2M is useful for this process step. Other useful acids include tetra fluoboric acid and dilute perchloric acid. Examples of acids that are not useful are 6M aqueous hydrochloric acid and 6M aqueous sulfuric acid, both of which dissolve or damage the photocatalytic titanium dioxide film on the glass. In the final process stage the glass may be rinsed, preferably with water, then dried.

#### **Properties of Self-Cleaning Glass**

The inventive self cleaning glasses include a substrate glass, barrier and a photocatalyst, as described above.

20 Self-cleaning glasses of the invention prepared as described above have coatings that strongly adhere to the glass and are abrasion resistant. These self-cleaning glasses have a photoefficiency, as defined in Example 1, when a film stearic acid is photoreacted, of at least  $3.5 \times 10^{-3}$ . In more general terms, the glasses of the invention have a photooxidation rate sufficient to oxidize daily, in direct sunlight, organic 25 contaminant films at a rate of 50 nm per day or more. At this rate, impaired vision due to a dirty windshield or lens of an eyeglass is minimized. 50 nm thick spots of contaminants interfere with vision, for example, by scattering light and causing glare. The glasses of the invention, as discussed more fully in Example 1, can also withstand successive applications and removals of scotch tape on their coated surfaces (tape test). Glasses of the invention can withstand being scribed with pencils of hardness H2 or softer as 30 described in Example 1.

### EXAMPLES

The invention may be further understood by reference to the following examples, which are not intended to limit the scope of the invention in any way.

5

#### Example 1

#### **Preparation of clear photoactive films of titanium dioxide on fused silica slides by spin coating**

Clear, approximately 60 nm thick films of titania were produced on fused silica by a sol-gel process. The sol was made of a precursor solution prepared by mixing 4.5 mL  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ , (97% in propanol) with 10.0 mL n-propanol and 1.6 mL acetylacetone (acac) to provide a stock solution having Ti:propanol:acac molar ratio of about 1:9:1.05. After aging for a week at room temperature (about 20°C - 25°C), a casting solution was prepared by mixing 1.0 ml of the precursor solution with a 1.8 ml water/n-propanol solution (1:9 v/v), the resulting water to titanium ratio being about 11:1. A clear, yellow casting solution, stable for at least two months and having a viscosity of 2.3 cp was obtained. Viscosity was measured using a falling ball type viscometer.

Prior to casting, the fused silica slides were rinsed in a cleaning solution (usually methanol), washed thoroughly with de-ionized water, and dried in a stream of air. The casting solution was then spread on the substrate (0.03 mL per 2.5x2.5 cm slide) which was spun, after the application, for 2 minutes at 4000 rpm to dryness. In the next stage, the coated silica slides were heated in air to 500°C at a rate of 50°C min<sup>-1</sup> and were calcined at this temperature for 30 minutes. The calcination transformed the product of the hydrolytic reaction into a microcrystalline oxide, stripped all organic residues, and bound the TiO<sub>2</sub> film to the substrate. Multiple TiO<sub>2</sub> layers were produced by applying a layer, drying in an oven (90°C, 10 minutes), applying another layer and finally calcining.

The process yielded uniform, clear and non-scattering films, as measured with a HP 8452A spectrometer (Figure 1). Comparison with the UV absorption spectrum of "milky" film coatings made of larger particles (Degussa P-25) revealed that the absorption edge of the clear films was shifted by 30-40 nm to the blue, as expected for nanoparticles in which electrons are confined.

The thickness of the films, 60±15 nm for a one layer film, was determined with an Alpha step 200 profilometer (Tencor Instruments). Transmission

electron diffraction patterns and images of the thin films were obtained using JEOL-1200EX and JEOL-2010 microscopes. For these measurements, the films were detached from their supports by pressing 200 mesh copper grids against the films while boiling in potassium hydroxide solution (6 M), following by thorough washing of the grids with water to remove any potassium residues. The electron diffraction ring patterns obtained by this method were indexed as that of  $\text{TiO}_2$  in the anatase phase and the dark field imaging suggested that the crystallites were segmented, with a typical segment being approximately 3 nm in diameter.

The resultant films were not damaged when wiped aggressively with any of several types of paper, including "Kimwipe", office copying machine paper, and newsprint, whether dry or wet. Furthermore, the films could not be removed by 20 successive applications and removals of Scotch® adhesive tape (3M-810), nor damaged when scribed with pencils of hardness H2 or softer.

The photoactivity of the various coated slides was tested by casting thin films of stearic acid ( $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ ) on the  $\text{TiO}_2$ -coated substrates and measuring at a defined irradiance the rate of decrease in the integrated absorbance of the ensemble of the C-H stretching vibrations between  $2700\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$ .

The measurements were performed on batches of 8-12 slides. The organic films were cast by applying  $3 \times 10^{-2}$  ml of  $8.8 \times 10^{-3}$  M stearic acid in methanol per slide and spinning at 1000 rpm for 2 minutes to dryness. The integrated IR absorbance of the stearic acid films was measured by a Nicolet Magna IR-750 FTIR. The actual number of stearic acid molecules on the surface was calculated based on the integrated absorbance of densely packed monolayers of homologs having a known area per molecule (such as octadecyl trichlorosilane, arachidic acid and behenic acid). A typical stearic acid film had, prior to illumination, an integrated absorbance of  $0.6\text{ cm}^{-1}$  corresponding to  $\sim 1.9 \times 10^{15}$  molecules  $\text{cm}^{-2}$ .

The UV light source for the photoefficiency measurements was either a UVA wide band lamp, the peak emission being at 365 nm (Hideaway 6000 Solarium, Helitron Ltd.) or a 254 nm line-emitting mercury lamp (Sylvania G30T3). The irradiance, measured at the slide surface, was  $2.4 \pm 0.4\text{ mW cm}^{-2}$  for the UVA source and  $0.8 \pm 0.15\text{ mW cm}^{-2}$  for the 254 nm source, corresponding to respective fluxes of

4.4x10<sup>15</sup> photons sec<sup>-1</sup> cm<sup>-2</sup> and 1.0x10<sup>15</sup> photons sec<sup>-1</sup> cm<sup>-2</sup>. These fluxes resulted in photocarrier generation rates differing only by a factor of 1.3, because of the large fraction of 254 nm UV photons absorbed in the 60 nm thick films in comparison to the lower fraction absorbed at the longer wavelength. The values given for the irradiance  
5 are the average between the readout of a JBA100 power meter and a second measurement by a well known photochemical method, potassium ferrioxalate actinometry.

Within the context of this application, the photoefficiency is defined as the number of carbon - hydrogen bonds of stearic acid stripped from the photocatalyst surface per incident photon,  $dA \times K \times N / f$ , where  $dA$  is the change in the integrated IR absorbance of the C-H vibrations of the stearic acid per minute;  $K$  is the number of C-H bonds in a stearic acid molecule (35);  $N$  is the number of stearic acid molecules per cm<sup>2</sup> per integrated absorbance unit, having a value of 3.17x10<sup>15</sup>; and  $f$  is the irradiance (2.6x 10<sup>17</sup> photons cm<sup>-2</sup> minute<sup>-1</sup> for the UVA source and 6x10<sup>16</sup> photons cm<sup>-2</sup>  
10 minute<sup>-1</sup> for the mercury lamp).

The integrated absorbance of the organic contaminant's infrared C-H stretching vibrations was measured as a function of the exposure time. Figure 2 presents the FTIR spectra of a TiO<sub>2</sub> film on silica contaminated with stearic acid prior to and after exposure to the UVA light for 7.5 minutes. In general, the rate at which the stearic acid film was stripped remained constant during the exposure, as long as a continuous stearic acid film remained on the surface of the photocatalyst. Thus, the efficiency of the photoreaction was generally independent of time, remaining constant throughout the reaction period. Table 1 presents the integrated absorbance of stearic acid on silica coated with the photoactive TiO<sub>2</sub> films following illumination with the  
20 UVA light. The efficiency in the table was calculated based on the change following 7.5 minutes of illumination.

The photoefficiency of a fused silica substrate coated with a single layer of TiO<sub>2</sub> film was between 14x10<sup>-3</sup> and 21x10<sup>-3</sup> upon illumination with the UVA light and between 45x10<sup>-3</sup> and 81x10<sup>-3</sup> upon illumination with the 254 nm light, the ratio  
30 between efficiencies being scaled with the ratio in the number of photons absorbed per

cm<sup>2</sup> per second at each wavelength. Values, averaged over more than 25 slides are presented in table 2.

**Table 1**

Slide No.	No. of TiO <sub>2</sub> layers	Integrated absorbance t=0	Integrated absorbance t=3.75 min.	Integrated absorbance t=7.5 min.	Integrated absorbance t=15 min.	efficiency
65	1	0.88		0.55	0.31	$18.8 \times 10^{-3}$
205	1	0.63	0.51	0.35	0.2	$15.9 \times 10^{-3}$
206	2	0.78	0.60	0.45	0.2	$18.8 \times 10^{-3}$
247	2	0.89	0.70	0.58	0.24	$17.6 \times 10^{-3}$
249	2	0.85	0.70	0.57	0.25	$15.9 \times 10^{-3}$

**Table 1:** Changes in the integrated absorbance of the FTIR C-H stretch band of stearic acid on silica slides coated with clear and photoactive TiO<sub>2</sub> upon illumination with UVA light. The efficiency given in the table was calculated based on the change after 7.5 minutes of exposure.

**Table 2**

	Glass substrate		Silica substrate	
	365 nm	254 nm	365 nm	254 nm
TiO <sub>2</sub> (clear) on non-etched substrate	$(0.7 \pm 0.35) \times 10^{-3}$	$(17.5 \pm 3.5) \times 10^{-3}$	$(17.5 \pm 3.5) \times 10^{-3}$	$(63 \pm 17.5) \times 10^{-3}$
TiO <sub>2</sub> (clear) on etched substrate	$(9.1 \pm 2.8) \times 10^{-3}$	$(58 \pm 18) \times 10^{-3}$	$(21 \pm 3.5) \times 10^{-3}$	$(73.5 \pm 28) \times 10^{-3}$

**Table 2:** Photoefficiency (number of C-H bonds consumed per impinging photon) of TiO<sub>2</sub> clear films on glass and on fused silica substrates, showing the effect of H<sub>2</sub>SO<sub>4</sub> etching of the substrate upon the efficiency. The values are averages for 20-30 samples.

**Example 2**  
**Preparation of clear photoactive films of titanium dioxide**  
**on soda lime glass slides by spin coating**

5 Clear, photoactive films of titanium dioxide were produced on soda lime glass (Corning 2947, composed of O (60 atom%), Si(24.5 atom%), Na(10 atom%), Ca(2.5 atom%), Mg(2 atom%), and Al(1 atom%)) by the sol-gel method described for Example 1. In the first step of their preparation, the substrates were cleaned by an organic solvent (usually methanol or chloroform), then etched by boiling them for at  
10 least 30 minutes in fuming 50% (9M) sulfuric acid at 240°C. After being cooled to ambient temperature, the slides were washed with de-ionized water and dried in a stream of air. Then, the same organotitanate coating solution described in Example 1 was applied onto the surface (0.04 ml per 3.75x2.5x1 mm slide) which was spun, as described for Example 1. The coated glass substrates, were calcined usually at a  
15 temperature of 400 °C, thus producing clear and homogeneous films, denoted as GE films. For comparison, TiO<sub>2</sub> films on non-etched glass slides, denoted as GN, and TiO<sub>2</sub> films on etched and on non-etched silica (denoted SE, SN respectively) were produced in the same manner. Thicker films were produced either by applying a first layer of the titanate precursor solution, oven drying (90 °C, 10 minutes), applying a  
20 second layer and calcination or by repeating the single layer preparation process. The former class is denoted as (2), whereas the latter is denoted as (1+1).

All films, whether GE, GN, SE, or SN withstood the abrasion tests described in Example 1. A ratio of BET (Brunauer-Emmett-Teller) to geometrical surface area of approximately 20 was determined for the TiO<sub>2</sub> coated glass slides by N<sub>2</sub>  
25 BET adsorption isotherms, using a Micromeritics AccuSorb system. Characterization of the films, i.e. UV, TEM and profilometry measurements were performed as described in Example 1. Figure 2 shows the UV absorption spectra of clear TiO<sub>2</sub> films on etched glass (dashed line) and on non-etched glass (solid line), the latter being blue shifted by 4-5 nm with respect to the former. As seen below, the difference between the spectra of  
30 films on etched glass (GN type) may have resulted of the GN type films not having the anatase phase or of smaller crystalline domains in the GN type films. "Plan view" TEM images of the TiO<sub>2</sub> films, detached from their substrates in the same manner as described in Example 1, revealed a distinct difference between type GE and type GN

films. Type GE films were found to be identical to the SN films described in Example 1 (i.e. consisted of segmented nanocrystallites having the anatase phase) whereas the type GN films were typical for materials having no long range order, with a diffused ring in their selected area diffraction pattern corresponding to an interplanar distance of 2.6 -3.6 Å.

The compositions of the supported films, as well as of the glass substrates, were measured by x-ray photoelectron spectroscopy (VG-ESCALAB). To obtain depth profiles, the samples were sputtered with an argon gun (Varian 981-2043, 3 kV, 25 mA) and re-measured. The estimated sputtering rate was 0.15 nm min.<sup>-1</sup>. For these measurements, the samples were cut into 8 mm x 8 mm slides, that were attached to their pedestals by a conducting adhesive tape to reduce charging during the sputtering process.

Table 3 presents the percentage of sodium atoms in various TiO<sub>2</sub> clear films on soda lime glass, and in glass slides, some pre-etched, some non-etched and some calcined after being etched, as deduced from the XPS measurements. These values are based on the area of the sodium and oxygen 1S peaks taking sensitivity factors (sf) of 2.51 and 0.63, respectively, and on the area of the 2P doublet (2P<sub>3/2</sub> + 2P<sub>1/2</sub>) peak of titanium, taking a sensitivity factor of 1.59. Whenever silicon was found, for example in the glass samples or after prolonged sputtering of the TiO<sub>2</sub> samples, its atomic fraction was calculated from its 2P peak (sf=0.17). No constituents apart from titanium, oxygen, and sodium were found in the TiO<sub>2</sub> films.

Table 3

Pre-treatment	Sputtering time (min.)	glass		TiO <sub>2</sub> on glass (one layer)		TiO <sub>2</sub> on glass (two layers)	
		Not calcined	calcined	untreated	HNO <sub>3</sub> treated	untreated	HNO <sub>3</sub> treated
Non-etched	0	7.2	35.0	21.5	2.0	14.0	2.5
	30						
	60			13.6			
	90	9.1	12.8		2.5		
	180	3.4	8.7	14.5			
	300	5.3		14.1			
Etched	420			17.1	18.0		
	0	1.8	7.5	8.4	3.2	7.7	0.0
	30	0.5			1.1		
	60			7.0			
	90		3.4				
	120			4.4			0.0
	150				1.6		
	300			3.0			

Atomic percentage (%) of sodium measured by XPS, in soda lime glass and in clear films of TiO<sub>2</sub> on soda lime glass.

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A high atomic fraction of sodium was measured not only at the interface between the TiO<sub>2</sub> and the glass but also at the air interface. The concentration of sodium at the air interface was actually higher than in the bulk of the films. Evidently, the sodium diffusion length exceeded the film thickness and sodium segregated at the surface of the titanium dioxide film. The effect of etching the glass prior to coating with the TiO<sub>2</sub> precursor on the sodium concentration at the TiO<sub>2</sub> film surface is evident, the atomic percentage of sodium in the GE films being 2-3 times lower than that in the GN films. In the GN films the atomic percentage of sodium exceeded that in the bulk of the soda lime glass (10 atom%), showing that the film was not only contaminated with sodium, but actually extracted sodium from the glass. The amount of sodium in the thicker photocatalyst films made by applying two layers of the organo-titanate precursor and then calcining, was only slightly smaller than in films made of one layer. A high atomic percentage (7.5%) of sodium was found on the glass surface after it was etched and calcined. Nevertheless, the fraction of sodium at the surface of the non-etched but calcined glass was far higher (35%). Thus, the pre-etching of the glass prior to application and calcining the photocatalyst precursor film caused effective blocking of sodium migration into the photocatalyst film.

20



The photoefficiency of the photocatalytic stearic acid stripping process, as defined in Example 1, was between  $5 \times 10^{-3}$  and  $12 \times 10^{-3}$  for the GE slides illuminated with the UVA light whereas for the  $\text{TiO}_2$  films made on non-etched glass (the GN films) it was at least 7 times less. The photoefficiency results obtained for a batch containing 12 slides, half of which were GE type while the other half were GN type are given as an example in Table 4. In Table 2 the average photoefficiencies obtained for  $\text{TiO}_2$  clear films on fused silica, on glass etched by  $\text{H}_2\text{SO}_4$  prior to coating with the titanium precursor, and on non-treated glass are presented. Each value listed in the table represents an average for more than 25 samples. For soda lime glass substrates, a large difference in the photoactivity was found between GE type and GN type samples, the latter being several times less efficient than the former. This difference was greater for excitation upon 365 nm photons than by 254 nm photons. In contrast to the observed difference in efficiency between films on etched and on non-etched glass, etching did not increase or reduce the photoactivity when the films were coated on fused silica.

TABLE 4

Slide No.	Pre-treatment	Photoefficiency (%)
398	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$4.9 \times 10^{-3}$
399	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$5.25 \times 10^{-3}$
400	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$8.4 \times 10^{-3}$
401	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$8.05 \times 10^{-3}$
402	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$7.7 \times 10^{-3}$
403	50% $\text{H}_2\text{SO}_4$ (boiled), 30 min.	$8.05 \times 10^{-3}$
404	without pre-treatment	$.35 \times 10^{-3}$
405	without pre-treatment	$.7 \times 10^{-3}$
406	without pre-treatment	$.7 \times 10^{-3}$
407	without pre-treatment	$.35 \times 10^{-3}$
408	without pre-treatment	$.35 \times 10^{-3}$
409	without pre-treatment	0.0
410	without pre-treatment	$.7 \times 10^{-3}$

The dependence of the efficiency of clear films of titanium dioxide on the calcination temperature is seen in Figure 4. In etched glass type (GE) films on soda lime glass, the efficiency decreased when the calcination temperature exceeded 450°C (B,C), whereas on fused silica no decrease in efficiency was observed at higher calcination temperatures (A). The absence of loss of efficiency in silica-supported films indicated that the cause of loss in the photoactivity was not sintering, leading to lower surface area. The results obtained with 254 nm light were similar, but the decrease in photoactivity of TiO<sub>2</sub> on soda lime glass upon calcination at elevated temperatures was less pronounced.

The effect of the duration of the etching in sulfuric acid at 240°C on the 365 and 254 nm photoefficiencies is seen in Figure 5. While etching for 10 minutes sufficed to produce a film which was highly photoactive under 254 nm light (filled circles), more than 45 minutes of etching were needed for best activity under 365 nm light (open circles).

Table 5

Batch number and (# of samples)	Film Type and wave-length	As is	Double calcination	NaNO <sub>2</sub> treatment	NaNO <sub>2</sub> treatment + calcination	NaOH soaking	NaOH soaking + calcination
1 (2)	P-25, 365 nm Degussa	$55.3 \times 10^3$	$40.6 \times 10^3$	$40.95 \times 10^3$	$9.45 \times 10^3$	$4.2 \times 10^{3b}$	$6.3 \times 10^{3b}$
2 (2)	P-25, 254 nm Degussa	$92.75 \times 10^3$	-	$136.85 \times 10^{3a}$	$33.6 \times 10^{3a}$	$75.6 \times 10^{3b}$	$10.15 \times 10^{3b}$
3 (2)	Etch glass, 4 layers, 365 nm.	$14 \times 10^3$	$14.35 \times 10^3$	$6.3 \times 10^{3a}$	$0.35 \times 10^{3a}$	0 <sup>b</sup>	0 <sup>b</sup>
4 (2)	Etch glass, 4 layers, 365 nm.	$12.25 \times 10^{3a}$	$13.65 \times 10^{3a}$	$9.1 \times 10^{3ac}$	$2.8 \times 10^{13ac}$	$10.85 \times 10^3$ b,c	0 <sup>bc</sup>
5 (1)	Etch glass, 4 layers, 365 nm.	$16.45 \times 10^3$	$12.6 \times 10^3$	$17.6 \times 10^{3d}$	$07.35 \times 10^{3d}$ $12.95 \times 10^{3d,c}$	-	-
6,7 (4)	Etch glass, 7 layers, 365 nm.	$18.2 \times 10^3$	-	-	$11.2 \times 10^{3f}$	-	$11.2 \times 10^{3d}$

Table 5: Photoefficiency of TiO<sub>2</sub> films, expressed as the number of C-H bonds in a steric acid film consumed per impinging photon.  
a-Dipping in NaNO<sub>2</sub> (1 M, 10 minutes, 20°C).  
b-Dipping in NaOH (1 M, 10 minutes, 20°C).  
c-Batch 4 obtained by washing batch 3 slides with methanol to remove stearic acid residues, immersion in water and drying.

d-Dipping in  $\text{NaNO}_3$  (0.2 M, 10 minutes,  $20^\circ\text{C}$ ).

e-Washing after calcination.

f-3 layers of  $\text{TiO}_2$ , calcination,  $\text{NaNO}_3$  layer by spin coating (0.2 M, 1250 rpm, 1 minute), calcination, washing and coating with 4 additional layers of  $\text{TiO}_2$ .

g-3 layers of  $\text{TiO}_2$ , calcination,  $\text{NaNO}_3$  layer by spin coating (0.2 M, 1250 rpm, 1 minute), calcination, washing and coating with 4 additional layers of  $\text{TiO}_2$ .

5

Table 5 demonstrates the deleterious effect of sodium contamination on the efficiency of titanium dioxide films on glass. Dipping of the clear  $\text{TiO}_2$  films in NaOH (1M,  $20^\circ\text{C}$ ) reduced their efficiency under 365 nm light to nil (Table 5, batch 3), and subsequent washing with de-ionized water led to recovery of the efficiency (Table 5, batch 4). However, when the NaOH treated slides were calcined, the loss of their efficiency could not be reversed (Table 5, batches 3,4). Double calcination of GE films (Table 5, batches 3-5) did not increase or decrease their efficiency. Films made of Degussa P-25 that were immersed in NaOH were 10 fold less efficient than untreated films, under 365 nm light (Table 5, batch 1). Immersion of P-25 samples in NaOH had, however, a less severe effect on their photoactivity at 254 nm (Table 5, batch 2). Untreated P-25 films showed a moderate decrease in efficiency upon a second calcination (Table 5, batch 1), possibly because their surface area was reduced.

Etched glass type (GE) films did not show a significant loss in photoefficiency at 365 nm after immersion in a 0.2M  $\text{NaNO}_3$  solution (Table 5, batches 3-5). Dipping in  $>1\text{M}$   $\text{NaNO}_3$  reduced, however, the 365 nm efficiency by  $\sim 50\%$ . The efficiency of films made of P-25 was reduced by dipping in 1M  $\text{NaNO}_3$  by 25% at 365 nm (Table 5, batch 1). No loss in efficiency was observed for 254 nm light (Table 5, batch 2). Films calcined following their immersion in  $\text{NaNO}_3$  had only 10-40% of the efficiency of untreated films under 365 nm light (Table 5, batches 3-5). The efficiency of the P-25 films subjected to the same treatment was only 20% of the efficiency of untreated films under UVA light (Table 5, batch 1), and 40% under 254 nm light (Table 5, batch 2). Washing with water after the calcination of  $\text{NaNO}_3$  treated GE films increased the efficiency of the calcined samples, probably by removing some of the sodium ions on the surface (Table 5, batch 4). In a sandwiched structure, where a  $\text{NaNO}_3$  layer, decomposing upon calcination to  $\text{Na}_2\text{O}$ , was introduced on a calcined  $\text{TiO}_2$  film made of 3 precursor layers, then covered with 4 layers of  $\text{TiO}_2$  precursor and

30

calcined, the efficiency was only 60% of the efficiency of clear films made of 7 precursor layers without  $\text{NaNO}_3$  (Table 5, batch 5).

To probe the effect of a second calcination, two batches of slides was prepared. In one the first precursor layer was applied to the etched glass, oven dried (90  
5 oC, 10 min.), coated with a second layer, then calcined. These slides were termed GE(2). The second batch was made by repeated coating and calcination of an etched glass slide. These slides were termed GE(1+1). The absorption spectra of the two batches were identical, showing that the sizes of the crystallites, their phases and the thickness of the films did not differ. The GE(1+1) films, despite being calcinated twice,  
10 did not show lesser photoactivity than the GE(2) films. When the glass was etched, then calcined (GC type samples) and then overcoated with the  $\text{TiO}_2$  precursor and re-calcined the efficiency was only 20-40% of that of the standard 1 layer GE film.

The XPS results show that sodium migrates from the soda lime glass substrate into the titanium dioxide layer during the calcination step. When the sodium  
15 was extracted from the surface of the soda lime glass, and when the extracted glass was overcoated with the organo-titanate precursor and calcined, then the sodium content in the titania films was significantly lower. Such lowering affected the titanium containing phase that formed and thereby the photocatalytic behavior. It is known that at temperatures below 550°C, the extraction of sodium from glass is governed by an ion  
20 exchange mechanism and is limited by the rate of the diffusion of sodium ions rather than by the rate of diffusion of protons. If the process of etching would not introduce a change in the glass structure and if charge neutrality would be maintained only through protonation of the originally sodium occupied sites, i.e. if a "hydrogen glass" would have formed, than calcination at 400°C should have resulted in complete recovery from  
25 the extraction, the  $\text{Na}^+$  being redistributed simply because of the higher  $\text{Na}^+$  diffusion coefficient at the calcination temperature of 400°C relative to that at the extraction temperature of 240°C ( $2 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$  versus  $2 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$  respectively, for a soda lime glass of similar composition). However, if the extraction of sodium and the formation of a "hydrogen glass" were followed by loss of water, then a layer of denser  
30 glass, containing fewer ion exchanging Si-OH functions and less permeable to  $\text{Na}^+$  ions would be formed. Formation of such a layer was proposed for dealkalization of soda

lime glass in atmospheres containing water vapor and  $\text{SO}_2$ . Such a sodium diffusion limiting layer is formed in glass by etching and calcination. Despite limiting the sodium diffusion, this layer does not completely prevent the migration of sodium, as is evident from the difference between the atomic percentage of sodium in etched glass prior to (1.8%) and after (7.5%) calcination. The results show that the atomic percentage of sodium in the surface layer of soda lime glass that was etched and then calcined was much smaller than in glass calcined without being etched (7.5% vs. 35% at the surface, and 3.4% vs. 12.8% after 90 minutes of argon sputter etching).

Depth profile measurements show a constant concentration of sodium across the  $\text{TiO}_2$  film in both GE type and GN type films, with an increase in the sodium concentration at the air interface. Apparently, the nanocrystalline  $\text{TiO}_2$  film has a greater affinity for sodium than the silicate network of soda lime glass, particularly when the surface of the crystallites is hydrated and the protons are sodium exchangeable,  $\text{H}_2\text{Ti}_n\text{O}_{2n+1}$  being a stronger acid than  $\text{H}_2\text{Si}_n\text{O}_{2n+1}$ . In silicate glasses, but not necessarily in  $\text{TiO}_2$  films on glass, sodium also accumulated at the surface upon hydration of the silicate network, sodium segregation at the surface being coupled with depletion of sodium from the layer below. The sodium depleted layer observed in silicate glasses was not observed in the GE films, showing that  $\text{Na}^+$  accumulated throughout the film, not only at its air interface.

It was particularly noteworthy that the concentration of sodium in the GN films was higher than in the soda lime glass itself. This higher concentration can be rationalized by  $\text{Ti-OH}$  being a stronger acid than  $\text{Si-OH}$ , because of the more electropositive nature of  $\text{Ti}^{+4}$  relative to  $\text{Si}^{+4}$ , combined with fast sodium diffusion across the film.

Because the sodium ions were uniformly redistributed by the  $400^\circ\text{C}$  calcination step, the ions diffusing rapidly through the nanocrystalline  $\text{TiO}_2$  layer, similar sodium concentrations in the "type GE" and the "type GN" films would have been observed, were it not for the existence of a sodium transport limiting layer at the  $\text{TiO}_2$  - extracted glass interface. The massive difference between the GE type and GN type films is explained by creation of a zone in the GE-type films through which sodium permeation was slow. When the precursor temperature is raised nucleation, crystal

growth, and oxidation of organic residues take place. The sodium concentration in the titanium dioxide film was not related to its final concentration at the glass-titania interface, but to its concentration at this interface at the start of the calcination, when the unique sodium diffusion limiting layer was formed. Sodium extraction followed by a first calcination, then by coating with the  $\text{TiO}_2$  precursor and by a final calcination did not provide films as photoactive as those obtained when in the first calcination the  $\text{TiO}_2$  precursor was already present. Therefore, dehydration and compacting of the glass accounted only for part of the sodium transport characteristics of the layer. The unique sodium transport limiting characteristics are explained by reaction of the decomposing anatase  $\text{TiO}_2$  precursor and the dehydrating hydrogen glass, and/or by fast nucleation and growth at the interface between the glass and the  $\text{TiO}_2$  precursor layer.

In the type GN films, in contrast with the type GE films, there was no long range order. Earlier work has shown that titanium dioxide films on non etched soda lime glass were of brookite phase when formed by rapid heating of a film of a hydrolyzed titanium alkoxide precursor ( $>25^\circ\text{C}/\text{min}$ ), and that a  $\text{Na}_2\text{O} \cdot x\text{TiO}_2$  phase was formed when the temperature was raised sufficiently slowly to allow diffusion of the sodium ions from the glass into the  $\text{TiO}_2$  layer. The absorption edge of  $\text{Na}_2\text{O} \cdot x\text{TiO}_2$  was found to be shifted by 10-12 nm to shorter wavelengths relative to the edge of anatase, whereas the absorption edge for the brookite structure was identical with that of anatase. the data did not reveal the existence of well defined phases in the GN films, possibly because a slowly polymerizing chelated precursor was used. Hence, sodium could diffuse into the nascent  $\text{TiO}_2$  film in amounts sufficient to prevent its crystallization.

The photoefficiency invariably decreased when the  $\text{Na}^+$  concentration increased in the  $\text{TiO}_2$  films. Furthermore, the photoactive GE films lost efficiency when soaked in  $\text{NaNO}_3$  and calcined at temperatures where the  $\text{NaNO}_3$  decomposed to sodium oxide. The lesser efficiency of films on soda lime glass relative to films on fused silica presented in Example 1 could have resulted either of the presence of non-anatase phases or the presence of sodium oxide at the air interface, where it would have raised the local pH. In films on non etched glass the sodium fraction exceeded 10 atom% and, as a result, formation of an ordered anatase, brookite or sodium titanate

phase was inhibited. This reduced the efficiency practically to nil for 365 nm illumination. In contrast, on etched glass there were only crystalline anatase domains, even though their sodium atom percentage was as high as 8%.

Because a sodium transport blocking layer forms of the hydrogen glass and the nascent, yet non-crystalline  $\text{TiO}_2$  layer, sodium diffusion takes place mainly during the beginning of the calcination process, and a second calcination has only a minor effect on the efficiency of the films (Table 5). That the critical step for prevention of sodium ion migration is the reaction of the hydrogen glass with the nascent  $\text{TiO}_2$  layer was also suggested by comparison of the efficiency of films prepared by two methods involving (a) applying a first layer, calcination, then applying a second layer and calcining again and (b) applying two successive layers and calcining only once. There was little or no difference in the photoefficiencies of the two films. The fact that the  $\text{TiO}_2$  film made on etched and calcined (GC type) glass had only 20-40% of the efficiency of a  $\text{TiO}_2$  film made by coating the precursor on etched but not calcined glass suggests that the sodium transport limiting layer, formed by interdiffusion of  $\text{TiO}_2$  and hydrogen glass, was a superior sodium transport blocker to the film formed on the dehydrated hydrogen glass.

Transport of sodium from the substrate into the photocatalyst film precursor and into the photocatalyst films is detrimental to their photocatalytic activity. The  $\text{TiO}_2$  films have a higher affinity for sodium ions than the soda lime glass itself and extract the sodium ions from the glass during the calcination step. Sodium transport to the  $\text{TiO}_2$  layer can be retarded by forming a blocking layer. Such a layer forms upon calcining the  $\text{TiO}_2$  precursor film on the hydrogen glass, formed upon extraction of the sodium with hot acids such as sulfuric acid.

### Example 3

#### Preparation of clear photoactive films of titanium dioxide with enhanced photoactivity on soda lime glass

Clear films of titanium dioxide were made on soda lime glass either with or without acid pre-treatment (types GE and GN respectively) as described in Example 2. Following their calcination, the samples were post-treated with dilute nitric acid,

usually by soaking them in 0.2 M  $\text{HNO}_3$  for 15 minutes at  $22 \pm 3^\circ\text{C}$ , then washed with water to remove acid residues.

In Table 3 the effect of post-treatment on the atomic percentage of sodium is presented. The atomic percentage of sodium in all films (GE(1), GN(1), GE(2), GN(2) as defined in Example 2) was reduced significantly by the post treatment. For example, from 8.4% to 3.2% at the surface of a titanium dioxide film on etched glass and from 21.5% to 2% at the surface of a  $\text{TiO}_2$  film on non-etched glass, manifesting the replacement of sodium ions in the films by protons from the acid.

Table 6 presents the efficiency (as defined in Example 1) measured for a batch of slides containing GN and GE slides, with and without post-treatment, upon illumination with the UVA source. In Table 6, pretreatment means boiling the uncoated glass in 9M sulfuric acid for 30 minutes. "without water wash" means that the slide was dried with a residue of nitric acid. "With water wash" means that any residual nitric acid was removed by washing with de-ionized water. The average efficiencies of slides with a post-treatment versus the average efficiencies without such a treatment are presented in Table 7. In Table 7, "treated with  $\text{HNO}_3$ " means soaked in  $\text{HNO}_3$  0.2 M for 15 minutes, followed by a water wash.

**Table 6**

Slide No.	Pre-treatment	Post-treatment	Photoefficiency (%) without water wash	Photoefficiency (%) with water wash
656	yes	yes	$14.7 \times 10^{-3}$	$10.15 \times 10^{-3}$
657	yes	yes	$14.0 \times 10^{-3}$	$11.9 \times 10^{-3}$
658	yes	no	$9.1 \times 10^{-3}$	$7.35 \times 10^{-3}$
659	yes	no	$7.0 \times 10^{-3}$	$7.35 \times 10^{-3}$
662	no	no	$1.05 \times 10^{-3}$	$1.05 \times 10^{-3}$
663	no	no	$0.35 \times 10^{-3}$	$0.35 \times 10^{-3}$
666	no	yes	$3.85 \times 10^{-3}$	$2.1 \times 10^{-3}$
667	no	yes	$3.15 \times 10^{-3}$	$1.75 \times 10^{-3}$



**Table 7**

	365 nm		254 nm	
substrate	non treated	treated with HNO <sub>3</sub>	non-treated	treated with HNO <sub>3</sub>
non-etched glass	$0.945 \times 10^{-3}$	$2.31 \times 10^{-3}$	$12.95 \times 10^{-3}$	$17.85 \times 10^{-3}$
etched glass	$8.4 \times 10^{-3}$	$9.8 \times 10^{-3}$	$56 \times 10^{-3}$	$64.4 \times 10^{-3}$

HNO<sub>3</sub> post-treatment significantly increased the photoefficiency of non-etched glass (GN type) TiO<sub>2</sub> films although their photoefficiency remained much smaller than that of the standard etched glass (GE) TiO<sub>2</sub> films. In GE type films the improvement was slighter. Evidently, post-treatment was not an effective substitute for pre-etching of the glass. The gain efficiency upon HNO<sub>3</sub> post treatment was partially lost with time, as observed in repeated measurements. No increase in efficiency was observed upon HNO<sub>3</sub> treatment of films prepared according to Example 1 on fused silica (Table 8), manifesting that the observed increase in efficiency in the TiO<sub>2</sub> coated glass was not due to a lowered surface pH. The cause of the improvement was reaction or neutralization of sodium oxide or its products that migrated to the titanium dioxide layer's surface during the calcination process.

**Table 8**

Slide No.	Slide Type	Post-Treatment	Photoefficiency(%)
a	TiO <sub>2</sub> /quartz	untreated	$14.7 \times 10^{-3}$
b	TiO <sub>2</sub> /quartz	untreated	$11.9 \times 10^{-3}$
c	TiO <sub>2</sub> /quartz	soaking in HNO <sub>3</sub> 0.2 M (22°C, 15 min.)	$12.6 \times 10^{-3}$
d	TiO <sub>2</sub> /quartz	soaking in HNO <sub>3</sub> 0.2 M (22°C, 15 min.)	$10.85 \times 10^{-3}$

For treating titanium dioxide films on soda lime glass, the acid chosen was nitric acid. The anion of this acid, in contrast to with the anions of sulfuric and

hydrochloric acid does not complex the four valent titanium ion. The rate of dissolution of the photoactive film in nitric acid was consequently much slower than its rate of dissolution in sulfuric or hydrochloric acid at the same normalities. Within this context, it is noteworthy that GE films were more resistant to soaking in concentrated acids than the GN films.

Soaking of the  $\text{TiO}_2$  films in dilute acids (like  $\text{HNO}_3$ ) reduced the concentration of sodium near the surface and improved the efficiency by exchanging sodium ions with protons without degrading the mechanical properties of the  $\text{TiO}_2$  films. The photoefficiency increased particularly in type GN films. Although such soaking was not an adequate substitute for etching the glass prior to the application of the titania precursor, it was an appropriate finishing step for the process of forming a photocatalytic film on soda lime glass.

#### Example 4

##### Preparation of clear photoactive films of titanium dioxide on soda lime glass from coating solutions having controlled viscosities

The coating solution prepared in the manner described in Example 1, (denoted as "Ti" solution in this example) was mixed with various non-interacting organic solvents such as hexane, methylene chloride, chloroform, thus obtaining coating solutions, their viscosities depending upon the volumetric ratio between the coating solution and the non-interacting solvent. For comparison, films made from the "Ti" solution, as well as from a mixture of the "Ti" solution with methanol which may interact, like other alcohols, with the titanium dioxide precursor, were prepared. The mixed solutions were spread on acid - etched glass substrates (40 ml per 3.75x2.5 cm) which were spun, after the application, in  $\text{N}_2$  environment, for 2 minutes at 1000, 2500 or 4000 rpm to dryness. The slides were then calcined at  $400^\circ\text{C}$  for 35 minutes, in air. Clear, homogenous, well adhered films, were obtained.

The photoefficiency of the various types of slides was measured simultaneously. The results are presented in Table 9. For spin coating at 1000 rpm, there was practically no adverse effect on the efficiency following coating by solutions containing a "Ti" / non-interacting solvents mixtures, despite the lower amount of  $\text{TiO}_2$  in these films, due to the reduced viscosity of the coating solution. For spin coating at

2500 rpm, films made of Ti / non-interacting solvents solutions had 30% - 45% of the efficiency of films made of the "Ti" solutions, when illuminated with 365 nm light, and app. 70% - 100% when illuminated with 254 nm light. In contrast, the efficiency, measured with 365 nm light, of TiO<sub>2</sub> films made of the Ti / methanol solution was only 6% of that of the regular GE film when coated at 2500 rpm and 62% when coated at 1000 rpm.

**Table 9**

Slide No.	Coating Solution (v/v)	Solution Viscosity (cp)	Spinning Rate (rpm)	Film Absorbance at 300 nm	Efficiency at 254 nm	Efficiency at 365 nm
1551	Ti/CH <sub>2</sub> Cl <sub>2</sub> (1:1)	0.82	1000	0.94	66.9x10 <sup>-3</sup>	10.9x10 <sup>-3</sup>
1552	Ti/hexane (1:1)	0.88	1000	0.88	81.9x10 <sup>-3</sup>	10.2x10 <sup>-3</sup>
1553	Ti/Chloroform (1:1)	1.16	1000	0.82	70.7x10 <sup>-3</sup>	8.4x10 <sup>-3</sup>
1554	Ti/methanol (1:1)	1.16	1000	0.58	64.1x10 <sup>-3</sup>	6.1x10 <sup>-3</sup>
1555	Ti	2.34	1000	1.09	80.2x10 <sup>-3</sup>	9.8x10 <sup>-3</sup>
1556	Ti/n-propanol (1:1)	1.96	1000	0.57	60.9x10 <sup>-3</sup>	7.4x10 <sup>-3</sup>
1559	Ti/methanol (1:1)	1.16	2500	0.50	43.1x10 <sup>-3</sup>	0.7x10 <sup>-3</sup>
1560	Ti/CH <sub>2</sub> Cl <sub>2</sub> (1:1)	0.82	2500	0.63	66.2x10 <sup>-3</sup>	4.2x10 <sup>-3</sup>
1561	Ti/hexane (1:1)	0.88	2500	0.62	64.4x10 <sup>-3</sup>	5.3x10 <sup>-3</sup>
1562	Ti/Chloroform (1:1)	1.16	2500	0.58	62.7x10 <sup>-3</sup>	3.5x10 <sup>-3</sup>
1563	Ti/n-propanol (1:1)	1.96	2500	0.49	43.8x10 <sup>-3</sup>	5.1x10 <sup>-3</sup>
1564	Ti	2.34	2500	0.71	65.1x10 <sup>-3</sup>	11.9x10 <sup>-3</sup>

Table 9: Efficiency values of slides prepared by spin coating of mixtures of the TiO<sub>2</sub> precursor coating solution with various non-interacting solvents. In the table, "Ti" represents the regular coating solution, its preparation being described in example 1.

It can be concluded that photoactive clear and homogenous films can be formed on glass by means of diluting the coating solution with solvents that do not interact with the titanium dioxide precursor and that this method is especially viable for cases in which relatively low rates of spinning are required.

**Example 5**  
**Preparation of clear photoactive films of titanium dioxide**  
**on soda lime glass by dip-coating**

Coating solutions of controlled viscosities, prepared in the manner described in example 4, were used to produce clear, photoactive and homogeneous films of  $\text{TiO}_2$  on glass. For that, corning 2947 soda lime glass slides, 7.5x2.5x0.1 cm in size, were etched as described in example 2, connected to a speed controlled elevator and dip coated with an up-stroke speeds ranging between  $0.5 \text{ cm min}^{-1}$  and  $4.3 \text{ cm min}^{-1}$ . The  $\text{TiO}_2$  precursor coated films were then calcined at  $400 - 450^\circ\text{C}$  for 35 minutes. A clear, homogeneous, well adhered film of  $\text{TiO}_2$ , was obtained. Best results, in terms of clarity and homogeneity, were obtained by performing the process under  $\text{N}_2$  atmosphere, enriched with the solvents' vapor. The photoefficiencies of several dip-coated films, as measured by the stearic acid test described in example 1, are presented in table 10.

A comparison between the photoefficiency of the dip - coated films (table 10) and films of similar thickness made by spin coating (Table 2) reveals that the efficiency of the dip-coated films was not inferior to that of the spin-coated films, thus enabling large scale implementation.

Table 10

Slide No.	Coating Solution (v/v)	Solution Viscosity (cp)	Dip-stroke Speed cm/min	Calcination	Film Absorbance at 300 nm	Efficiency at 365 nm
1636	Ti/hexane (1:1)	0.88	4.3	400°C, 35 min.	0.65	$12.3 \times 10^{-3}$
1667	Ti/hexane (1:1)	0.88	2.68	450°C, 35 min.	0.57	$11.0 \times 10^{-3}$
1664	Ti <sup>#</sup> /hexane (1:1)	0.9	3.22	450°C, 35 min.	0.55	$9.1 \times 10^{-3}$
1666	Ti/hexane (2:3)	1.02	1.34	450°C, 35 min.	0.61	$8.8 \times 10^{-3}$
1650	Ti/hexane (2:3)	1.02	0.54	450°C, 35 min.	1.13	$13.7 \times 10^{-3}$
1623	Ti/hexane (3:7)	0.66	4.3	400°C, 35 min.	0.28	$5.6 \times 10^{-3}$
1655	Ti <sup>#</sup> /hexane (3:7)	0.65	0.54 (2 layers)	450°C, 35 min.	1.00	$14 \times 10^{-3}$

Table 10: Efficiency values of slides prepared by dip-coating in mixtures hexane and the TiO<sub>2</sub> precursor coating solution. In the table, "Ti" represents the regular coating solution, the water to titanium ratio being 11:1, while Ti<sup>#</sup> represents a coating solution where the water to titanium ratio was app. 4:1

#### Example 6

##### Preparation of clear photoactive films of titanium dioxide with sodium diffusion limiting layer

Silica films were produced on soda lime glass by the same manner described in Examples 1 and 2, using silicon tetrapropoxide instead of titanium tetra-i-propoxide. Here, the silicate precursor solution consisted of 10 ml n-propanol, 1.6 ml acetylacetonate (acac) and 4.9 ml of a Si(OPr)<sub>4</sub> solution (Aldrich Cat. No. 23,574, 95% by weight). The coating solution was made from 1.0 ml of the silicate precursor solution and 1.8 ml of 1:10 (v:v) water in n-propanol. 3.75 cm x 2.5 cm x 1 mm soda lime glass slides were then etched in boiling sulfuric acid for 30 minutes as described in Example 2, and coated by spin coating as described therein. Following drying at 80°C for 20 minutes, a second layer, made of the same coating solution described in Example

1 (denoted as "overlayer"), was applied by spin coating as described therein. The slides were then calcined at 450°C for 30 minutes to produce clear films comprised of a silica layer (denoted as "underlayer") between the glass substrate and the photoefficient titanium dioxide overlayer. Glass slides coated with a film containing a first layer of zirconia and a second, photoactive layer of titania were obtained in the same manner. Here, the zirconia coating solution was made of zirconium tetra n-propoxide (Aldrich 33,397 -2, 70% in 1-propanol) with the same molar ratios between zirconium, acac, water and propanol as described for the titania precursor coating solution in Example 1. No post-treatment with nitric acid was used.

The efficiency of the slides was measured in the manner described in Example 1. For comparison, films containing one and two layers of TiO<sub>2</sub> on glass, were made from the same batch of etched glass slides and with the same TiO<sub>2</sub> precursor coating solution. The efficiency of these slides was measured simultaneously with that of the glass-silica-titania films. As shown in Table 11, the efficiency of the two layered structure, containing a silica underlayer and TiO<sub>2</sub> overlayer, was higher than that of a single layer of titanium dioxide by a factor of between 1.4 and 2.0, but less than that of a film containing two layers of TiO<sub>2</sub>.

**Table 11**

Slide No.	Structure	Photoefficiency
701	1 layer of TiO <sub>2</sub> on soda lime glass	$3.5 \times 10^{-3}$
706	1 layer of TiO <sub>2</sub> on soda lime glass	$5.6 \times 10^{-3}$
709	1 layer of TiO <sub>2</sub> on a silica underlayer applied on soda lime glass	$8.75 \times 10^{-3}$
710	1 layer of TiO <sub>2</sub> on a silica underlayer applied on soda lime glass	$10.85 \times 10^{-3}$
699	2 layers of TiO <sub>2</sub> on soda lime glass	$14.35 \times 10^{-3}$
712	2 layers of TiO <sub>2</sub> on soda lime glass	$12.95 \times 10^{-3}$
713	2 layers of TiO <sub>2</sub> on soda lime glass	$12.6 \times 10^{-3}$

A two-layered structure, consisting of a zirconia underlayer and one TiO<sub>2</sub> overlayer coated on glass, had higher efficiency than that of a glass coated with a single film of TiO<sub>2</sub>, when made at calcination temperatures higher than 500°C, where the

diffusion of sodium into the forming  $\text{TiO}_2$  film is fast enough to reduce its efficiency even in acid etched glass substrates (Figure 4). This makes such a sodium diffusion blocking structure appropriate for applications where the glass has to withstand high temperatures, for example in products made by tempering of the glass.

### Example 7

#### Preparation of clear photoactive films of titanium dioxide on a layer made of a mixture of a $\text{TiO}_2$ precursor and a $\text{SiO}_2$ precursor

A layer composed of a mixture of  $\text{TiO}_2$  and  $\text{SiO}_2$  (1:1) molar ratio was produced on soda lime glass and on fused silica by preparing the appropriate coating solution and applying it onto the substrate by spin coating as described in examples 1 and 2. A precursor solution was made of 10 ml n-propanol, 2.25 ml titanium-tetra-i-propoxide (98% in propanol, density: 1.033 gr.  $\text{cm}^{-3}$ ), 1.6 ml acetylacetonate (aac) and 2.43 ml of silicon tetrapropoxide (Aldrich 23,574-1, 95% in propanol, density: 0.916 gr.  $\text{cm}^{-3}$ ). After aging the precursor solution for a day, the coating solution was made by mixing 1.0 ml of the mixed precursor solution with 1.8 ml of a water/ n-propanol solution (1:10 v/v). The coating solution was then spread by spin coating at 4000 rpm on  $\text{H}_2\text{SO}_4$  etched glass slides (40  $\mu\text{l}$  per 3.75 x 2.5 cm slide) and on non-etched fused silica slides (30  $\mu\text{l}$  per 2.5 x 2.5 cm slide). The slides were then dried in an oven at 100°C for 10 minutes. On part of the slides, a second layer, consisting of the  $\text{TiO}_2$  precursor coating solution, mentioned in Example 1, was applied in the same manner described in Examples 1,2. For reference, several other etched glass and fused silica slides were coated with two layers of the same  $\text{TiO}_2$  precursor coating solution without being coated with the mixed underlayer. All slides were then calcined at 450°C for 30 minutes to produce clear, well adhered films. No post-treatment with nitric acid was used.

The efficiency of the slides was measured in the manner described in Example 1. The films made of the  $\text{TiO}_2/\text{SiO}_2$  mixture were totally inactive. However, films consisting of a  $\text{TiO}_2$  overlayer on an inactive underlayer consisting of  $\text{TiO}_2/\text{SiO}_2$  were found to be between 50% and 100% more efficient than films made of one layer of  $\text{TiO}_2$ , regardless of the substrate (Table 12).

Table 12

Slide No.	Substrate	Structure	Efficiency
A	Fused Silica	Mixed $\text{SiO}_2/\text{TiO}_2$ (1:1) layer	$0.3 \times 10^{-3}$
B	Fused Silica	Mixed $\text{SiO}_2/\text{TiO}_2$ (1:1) layer	$1.7 \times 10^{-3}$
C	Fused Silica	One layer of $\text{TiO}_2$ on a mixed $\text{SiO}_2/\text{TiO}_2$ (1:1) layer	$13.7 \times 10^{-3}$
D	Fused Silica	One layer of $\text{TiO}_2$ on a mixed $\text{SiO}_2/\text{TiO}_2$ (1:1) layer	$16.1 \times 10^{-3}$
E	Fused Silica	One layer of $\text{TiO}_2$	$4.9 \times 10^{-3}$
F	Fused Silica	One layer of $\text{TiO}_2$	$9.0 \times 10^{-3}$
G	Fused Silica	Two layers of $\text{TiO}_2$	$13.1 \times 10^{-3}$
H	Fused Silica	Two layers of $\text{TiO}_2$	$17.2 \times 10^{-3}$
684	Etched Glass	Mixed $\text{SiO}_2/\text{TiO}_2$ (1:1) layer	$0.0 \times 10^{-3}$
685	Etched Glass	Mixed $\text{SiO}_2/\text{TiO}_2$ (1:1) layer	$0.0 \times 10^{-3}$
1711	Etched Glass	One layer of $\text{TiO}_2$ on a mixed $\text{SiO}_2/\text{TiO}_2$ (1:1) layer	$16.6 \times 10^{-3}$
1712	Etched Glass	One layer of $\text{TiO}_2$ on a mixed $\text{SiO}_2/\text{TiO}_2$ (1:1) layer	$16.7 \times 10^{-3}$
1701	Etched Glass	One layer of $\text{TiO}_2$	$8.6 \times 10^{-3}$
1702	Etched Glass	One layer of $\text{TiO}_2$	$8.6 \times 10^{-3}$
1707	Etched Glass	Two layers of $\text{TiO}_2$	$18.7 \times 10^{-3}$
1708	Etched Glass	Two layers of $\text{TiO}_2$	$17.4 \times 10^{-3}$

Table 12: The photoefficiencies of films composed of one  $\text{TiO}_2$  layer on a silica/titania underlayer in comparison to films made of one  $\text{TiO}_2$  layer, two  $\text{TiO}_2$  layers, and a mixture of  $\text{TiO}_2/\text{SiO}_2$ .



**We claim:**

1. A process for the manufacture of self-cleaning glass, comprising:  
applying to glass a photocatalyst precursor composition to form a  
5 photocatalyst-containing film; and  
impeding migration of alkali metal ions or alkali metal oxide from the  
glass into the photocatalyst precursor or film.
2. A process for the manufacture of self-cleaning glass, comprising:  
10 applying to glass a barrier, said barrier preventing or slowing migration  
of alkali metal ions or alkali metal oxide from the glass; and  
forming on said barrier a photocatalyst-containing film.
3. A process for the manufacture of self-cleaning glass, comprising:  
15 applying to an etched, acid glass a photocatalyst precursor composition,  
to form a photocatalyst-containing film.
4. A process for the manufacture of self-cleaning glass, comprising:  
20 applying to glass a film formed of a precursor of  $\text{TiO}_2$  and a precursor of  
an oxide of a 3, 4, or 5-valent element, which oxide is solid at about  $300^\circ\text{C}$ ; and  
forming on said film a photocatalyst-containing film.
5. A process for the manufacture of self-cleaning glass, comprising:  
25 applying to an acid glass a first film, the first film formed from a  
precursor of an oxide of a 3, 4, or 5-valent element, wherein the element is titanium,  
zirconium, tungsten, tin, silicon, or combination thereof; and  
forming on said first film a photocatalyst-containing second film.
6. A process for the manufacture of self-cleaning glass, comprising:  
30 applying to acid glass a film comprising a reaction product of the  
acid glass and a precursor of a 3, 4, or 5-valent form of titanium, zirconium, tungsten,  
tin, silicon, or combination thereof; and

forming on said barrier a photocatalyst-containing film.

7. A process for the manufacture of self-cleaning glass, comprising:

treating glass to form acid glass;

5 applying a photocatalyst-precursor to the acid glass to form a coated glass;

calcining the coated glass to form a photocatalytically active, self-cleaning glass.

10 8. A process according to any of claims 1-7, wherein said photocatalyst comprises a photoconductor or semiconductor with a band gap in the range of 2.5 eV to 4.5 eV.

9. The process according to any of claims 1-7, wherein said photocatalyst comprises titanium, zirconium, tungsten, tin, or molybdenum.

15

10. A process according to any of claims 1-7, wherein said photocatalyst comprises titanium dioxide.

20 11. A process according to claim 10, wherein at least a portion of said titanium dioxide is in anatase phase.

12. The process of any of claims 1-6, further comprising the step of:  
calcining the photocatalyst film-coated glass to form a photocatalytically active, self-cleaning glass.

25

13. A process according to any of claims 1-7, wherein said glass comprises soda lime glass.

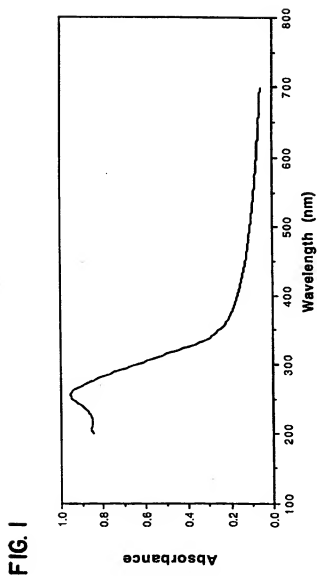
30 14. A process according to claim 6, wherein said precursor comprises a precursor of titanium dioxide.

15. A process according to claim 6, wherein said precursor comprises a precursor of zirconium dioxide.
16. A process according to claim 6, wherein said precursor comprises a precursor of silicon dioxide.
17. A self-cleaning glass comprising:  
a glass;  
a photocatalyst-containing film formed on the glass from a photocatalyst precursor; and  
a barrier impeding migration of alkali metal ions or alkali metal oxides into the photocatalyst precursor or film.
18. A self-cleaning glass comprising:  
a glass;  
a photocatalyst-containing film formed on the glass by acid etching the glass and applying to the acid glass a photocatalyst precursor.
19. A self-cleaning glass comprising:  
a glass;  
a first film formed on the glass of a precursor of  $\text{TiO}_2$  and a precursor of an oxide of 3, 4, or 5-valent element, which oxide is solid at about  $300^\circ\text{C}$ ; and  
a photocatalyst-containing second film formed on the first film.
20. A self-cleaning glass comprising:  
a glass;  
a first film formed on the glass of a precursor of an oxide of a 3, 4, or 5-valent element, wherein the element comprises titanium, zirconium, tungsten, tin, silicon, or combination thereof; and  
a photocatalyst-containing second film formed on the first film.

21. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst comprises a photoconductor or semiconductor with a band gap in the range of 2.5 eV to 4.5 eV.
- 5 22. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst comprises titanium, zirconium, tungsten, tin, or molybdenum.
23. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst comprises titanium dioxide.
- 10 24. A self-cleaning glass according to claim 23, wherein at least a portion of said titanium dioxide is in anatase phase.
25. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst precursor is calcined on the glass to form a photocatalytically active, self-cleaning glass.
- 15 26. A self-cleaning glass according to any of claims 17-20, wherein said glass comprises soda lime glass.
- 20 27. A self-cleaning glass according to any of claims 19-20, wherein said precursor of the 3, 4, or 5-valent element oxide comprises a precursor of zirconium dioxide.
28. A self-cleaning glass according to any of claims 19-20, wherein said precursor of the 3, 4, or 5-valent element oxide comprises a precursor of silicon dioxide.
- 25 29. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst precursor comprises titanium tetraalkoxide.
- 30 30. A self-cleaning glass according to any of claims 17-20, wherein said photocatalyst precursor comprises a complex of titanium tetraalkoxide with acetylacetone.

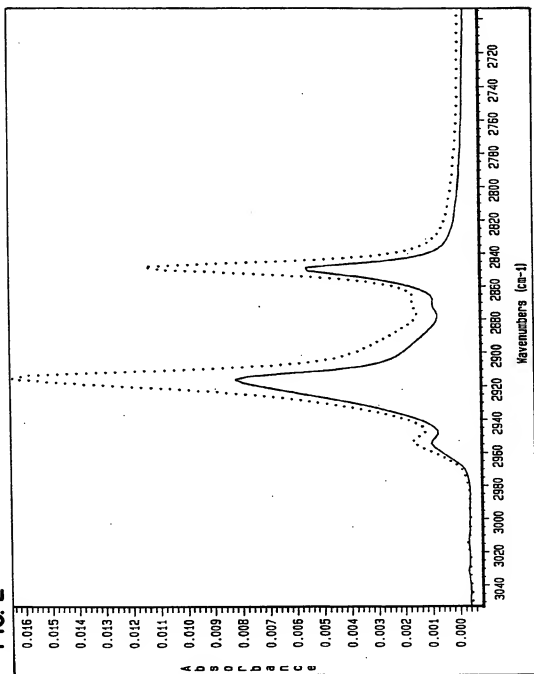
31. A self-cleaning glass according to claim 17, wherein said barrier comprises a reaction product of the glass and the photocatalyst precursor, the glass being etched to form an acid glass prior to the reaction with the precursor.

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FIG 2



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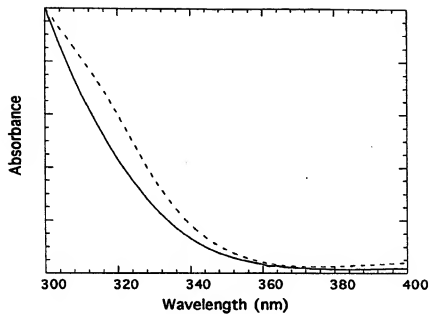


FIG. 3

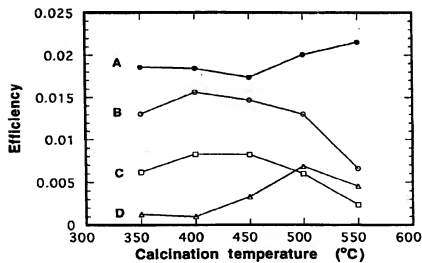


FIG. 4



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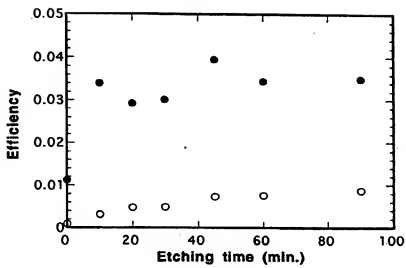


FIG. 5

## INTERNATIONAL SEARCH REPORT

 International Application No.  
 PC1/US 96/12792

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C03C17/34 C03C17/25 C03C23/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 684 075 (TOTO LTD) 29 November 1995	1,2, 8-13,17, 21-26, 29,30
P,Y	see page 9, line 7 - line 36; example 35	3,7,18, 31
X	& WO,A,95 15816 (TOTO LTD) 15 June 1995	1,2, 8-13,17, 21-26, 29,30
Y	---	3,7,18, 31
Y	GB,A,2 206 878 (GLAVERBEL) 18 January 1989	3,7,18, 31
	see abstract	
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 November 1996

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 625 (C-1279), 29 November 1994 & JP,A,06 239650 (NIPPON TAISANBIN KOGYO KK), 30 August 1994, see abstract ---	1-31
A	EP,A,0 174 727 (PILKINGTON BROTHERS PLC) 19 March 1986 see abstract ---	1-31
A	SZKLO I CERAMIKA, vol. 43, no. 6, 1992, POLAND, pages 2-7, XP002018688 ZELAZOWSKA: "Study of metal oxide and titanium oxynitride coatings on soda-lime glass" see page 5, left-hand column see page 7, left-hand column -----	1-31

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 96/12792

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Get Now: ☒ PDF | [File History](#) | [Other choices](#)Tools: Add to Work File: [Create new Work File](#)View: [Expand Details](#) | [INPADOC](#) | Jump to: [Top](#)☒ Go to: [Derwent](#)☒ [Email this](#)Title: **WO9710186A1: PHOTOCATALYTIC COATING SUBSTRATE** [\[French\]](#)Derwent Title: Self-cleaning photocatalytic coating - of crystalline titanium oxide for glass, ceramic or glass-ceramic substrate [\[Derwent Record\]](#)Country: **WO** World Intellectual Property Organization (WIPO)Kind: **A1** Publ. of the Int. Appl. with Int. search report <sup>1</sup>Inventor: **BOIRE, Philippe**; 77, rue de Cambonne, F-75015 Paris, France  
**TALPAERT, Xavier**; 184, rue de Belleville, F-75020 Paris, FranceAssignee: **SAINT-GOBAIN VITRAGE**, 18, avenue d'Alsace, F-92400 Courbevoie, FranceCorporate Tree data: [Compagnie de Saint-Gobain \( STGOBAIN \)](#);  
[News, Profiles, Stocks and More about this company](#)Published / Filed: **1997-03-20 / 1996-09-13**Application Number: **WO1996FR0001421**IPC Code: Advanced: **C03C 17/00; C03C 17/25; C03C 17/34; C04B 41/45; C04B 41/52; C04B 41/81; C04B 41/89; G02F 1/1333; G02F 1/1335; G02F 1/153; G02F 1/157; G02F 1/01; more...**  
IPC-7: **C03C 8/20; C03C 17/00; C03C 17/34;**ECLA Code: **C03C17/00B2; C03C17/00D2; C03C17/25C; C03C17/34D2; C03C17/34D4D; C04B41/45B30; C04B41/52; C04B41/81; C04B41/89; G02F1/1333;**Priority Number: **1995-09-15 FR1995000010839**Abstract: The invention relates to a glass-, ceramic- or vitro-ceramic-based substrate (1) having on at least a portion of at least one of its sides a coating (3) with photocatalytic characteristics comprising titanium oxide which is at least partially crystallized. It also relates to applications of such substrates and its production process. L'invention a pour objet un substrat (1) a base verriere, ceramique ou vitro-ceramique, muni sur au moins une partie d'au moins une de ses faces d'un revetement (3) a propriete photocatalytique comportant de l'oxyde de titane au moins partiellement cristallise. Elle concerne egalement les applications d'un tel substrat et son mode d'obtention. [\[French\]](#)

Representative

Image:

Attorney, Agent or Firm: **RENOUS-CHAN, Veronique**;

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AL AU BB BG BR CA CN CZ EE GE HU IL IS JP KE KP KR LK LR LS  
LT LV MG MK MN MW MX NO NZ PL RO SD SG SI SK TR TT UA  
UG US VN, **European patent:** AT BE CH DE DK ES FI FR GB GR IE  
IT LU MC NL PT SE, **OAPI patent:** BF BJ CF CG CI CM GA GN ML  
MR NE SN TD TG, **ARIPO patent:** KE LS MW SD SZ UG,  
**Eurasian patent:** AM AZ BY KG KZ MD RU TJ TM

Family: [Show 46 known family members](#)

First Claim: [Show all claims](#)  
REVENDIGATIONS 1. Substrat (1) à base verrière, céramique ou vitro- céramique, muni sur au moins une partie d'au moins une de ses faces d'un revêtement (3) à propriété photo-catalytique comportant de l'oxyde de titane au moins partiellement cristallisé.

Description  
[Expand description](#)

#### ± SUBSTRAT A REVETEMENT PHOTOCATALYTIQUE 5













L'invention concerne des substrats à base verrière, céramique ou vitro- céramique, plus particulièrement en verre, notamment transparents, que l'on munit de revêtements à propriétés photo-catalytiques, en vue de fabriquer des vitrages d'applications diverses, comme les vitrages utilitaires, vitrages pour véhicules ou pour bâtiments.

De plus en plus, on cherche à fonctionnaliser les vitrages en déposant à leur surface des couches minces destinées à leur conférer une propriété particulière selon l'application visée. Ainsi, il existe des couches à fonction optique, comme les couches dites anti-reflet composées d'un empilement de couches alternativement à haut et bas indices de réfraction. Pour une fonction anti-statique, ou chauffante du type anti-givre, on peut aussi prévoir des couches minces conductrices électriquement, par exemple à base de métal ou d'oxyde métallique dopé. Pour une fonction thermique, de bas-émissivité ou anti-solaire par exemple, on peut se tourner vers des couches minces en métal du type argent ou à base de nitrure ou d'oxyde métallique. Pour obtenir un effet « anti-pluie », peuvent être prévues des couches à caractère hydrophobe, par exemple à base d'organo-silane fluoré. Cependant, il existe encore un besoin pour un substrat, notamment un vitrage que l'on pourrait qualifier « d'anti-salissures », c'est-à-dire visant la permanence dans le temps des propriétés d'aspect et de surface, et permettant notamment d'espacer les nettoyages et/ou d'améliorer la visibilité, en parvenant à éliminer au fur et à mesure les salissures se déposant progressivement à la surface du substrat, notamment les salissures d'origine organique comme les traces de doigts ou des produits organiques volatils présents dans l'atmosphère, ou même des salissures du type buée.

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References:

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<a href="#">PDF</a>	<a href="#">DE10158433B4</a>	2006-05-18	Sepeur, Stefan, Dr.	NANO-X GmbH	Beschichtung
<a href="#">PDF</a>	<a href="#">US6939611</a>	2005-09-06	Fujishima; Akira	Kanagawa Academy of Science and Technology	Window glass employing titanium dioxide photocatalyst
<a href="#">PDF</a>	<a href="#">US6875319</a>	2005-04-05	Nadaud; Nicolas	Saint-Gobain Glass France	Substrate with photocatalytic coating
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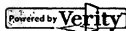
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	US6027766	2000-02-22	Greenberg; Charles B.	PPG Industries Ohio, Inc.	Photocatalytically-activated cleaning article and method making same

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<b>(51) Classification internationale des brevets <sup>6</sup> :</b> <b>C03C 17/00, 8/20, 17/34</b>	<b>A1</b>	<b>(11) Numéro de publication internationale: WO 97/10186</b> <b>(43) Date de publication internationale: 20 mars 1997 (20.03.97)</b>
<b>(21) Numéro de la demande internationale:</b> PCT/FR96/01421 <b>(22) Date de dépôt international:</b> 13 septembre 1996 (13.09.96) <b>(30) Données relatives à la priorité:</b> 95/10839 15 septembre 1995 (15.09.95) FR <b>(71) Déposant (pour tous les Etats désignés sauf US):</b> SAINT-GOBAIN VITRAGE [FR/FR]; 18, avenue d'Alsace, F-92400 Courbevoie (FR). <b>(72) Inventeurs; et</b> <b>(75) Inventeurs/Déposants (US seulement):</b> BOIRE, Philippe [FR/FR]; 77, rue de Cambronne, F-75015 Paris (FR). TALPAERT, Xavier [FR/FR]; 184, rue de Belleville, F-75020 Paris (FR). <b>(74) Mandataire:</b> RENOUS-CHAN, Véronique; Saint-Gobain Recherche, 39, quai Lucien-Léfranc, F-93300 Aubervilliers (FR).		<b>(81) Etats désignés:</b> AL, AU, BB, BG, BR, CA, CN, CZ, EE, GE, HU, IL, IS, JP, KE, KP, KR, LK, LR, LS, LT, LV, MG, MK, MN, MW, MX, NO, NZ, PL, RO, SD, SG, SI, SK, TR, TT, UA, UG, US, VN, brevet ARIPO (KE, LS, MW, SD, SZ, UG), brevet eurasién (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), brevet OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Publiée</b> <i>Avec rapport de recherche internationale.</i> <i>Avant l'expiration du délai prévu pour la modification des revendications, sera republiée si de telles modifications sont reçues.</i>

(54) Title: PHOTOCATALYTIC COATING SUBSTRATE

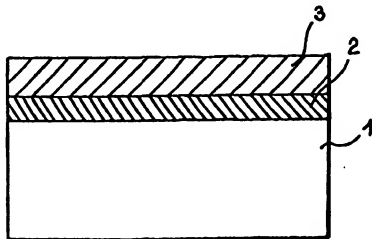
(54) Titre: SUBSTRAT A REVETEMENT PHOTOCATALYTIQUE

(57) Abstract

The invention relates to a glass-, ceramic- or vitro-ceramic-based substrate (1) having on at least a portion of at least one of its sides a coating (3) with photocatalytic characteristics comprising titanium oxide which is at least partially crystallized. It also relates to applications of such substrates and its production process.

(57) Abrégé

L'invention a pour objet un substrat (1) à base verrière, céramique ou vitro-céramique, muni sur au moins une partie d'au moins une de ses faces d'un revêtement (3) à propriété photocatalytique comportant de l'oxyde de titane au moins partiellement cristallisé. Elle concerne également les applications d'un tel substrat et son mode d'obtention.





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**SUBSTRAT A REVETEMENT PHOTOCATALYTIQUE**

5

L'invention concerne des substrats à base verrière, céramique ou vitro-céramique, plus particulièrement en verre, notamment transparents, que l'on munit de revêtements à propriétés photo-catalytiques, en vue de fabriquer des vitrages d'applications diverses, comme les vitrages utilitaires, vitrages pour véhicules ou pour bâtiments.

De plus en plus, on cherche à fonctionnaliser les vitrages en déposant à leur surface des couches minces destinées à leur conférer une propriété particulière selon l'application visée. Ainsi, il existe des couches à fonction optique, comme les couches dites anti-reflet composées d'un empilement de couches alternativement à haut et bas indices de réfraction. Pour une fonction anti-statique, ou chauffante du type anti-givre, on peut aussi prévoir des couches minces conductrices électriquement, par exemple à base de métal ou d'oxyde métallique dopé. Pour une fonction thermique, de bas-émissivité ou anti-solaire par exemple, on peut se tourner vers des couches minces en métal du type argent ou à base de nitrure ou d'oxyde métallique. Pour obtenir un effet « anti-pluie », peuvent être prévues des couches à caractère hydrophobe, par exemple à base d'organo-silane fluoré ...

Cependant, il existe encore un besoin pour un substrat, notamment un vitrage que l'on pourrait qualifier « d'anti-salissures », c'est-à-dire visant la permanence dans le temps des propriétés d'aspect et de surface, et permettant notamment d'espacer les nettoyages et/ou d'améliorer la visibilité, en parvenant à éliminer au fur et à mesure les salissures se déposant progressivement à la surface du substrat, notamment les salissures d'origine organique comme les traces de doigts ou des produits organiques volatils présents dans l'atmosphère, ou même des salissures du type buée.

Or on sait qu'il existe certains matériaux semi-conducteurs, à base d'oxyde métallique, qui sont aptes, sous l'effet d'un rayonnement de longueur d'onde adéquate, à initier des réactions radicalaires provoquant l'oxydation de produits organiques : on parle en général de matériaux « photo-catalytiques » ou encore « photo-réactifs ».

L'invention a alors pour but la mise au point de revêtements photo-catalytiques sur substrat, qui présentent un effet « anti-salissures » marqué vis-à-vis du substrat et que l'on puisse fabriquer de manière industrielle.

L'invention a pour objet un substrat à base verrière, céramique ou vitro-céramique, notamment en verre et transparent, muni sur au moins une partie d'au moins une de ses faces d'un revêtement à propriété photo-catalytique comportant de l'oxyde de titane au moins partiellement cristallisé. L'oxyde de titane est cristallisé de préférence « in situ », lors de la formation du revêtement sur le substrat.

L'oxyde de titane fait en effet partie des semi-conducteurs qui, sous l'action de la lumière dans le domaine visible ou des ultraviolets, dégradent des produits organiques qui se déposent à leur surface. Choisir l'oxyde de titane pour fabriquer un vitrage à effet « anti-salissures » est donc particulièrement indiqué, et ce d'autant plus que cet oxyde présente une bonne résistance mécanique et chimique : pour être efficace longtemps, il est évidemment important que le revêtement conserve son intégrité, alors même qu'il se trouve directement exposé à de nombreuses agressions, notamment lors du montage du vitrage sur chantier (bâtiment) ou sur ligne de production (véhicule), ce qui implique des manipulations répétées par des moyens de préhension mécaniques ou pneumatiques, et également une fois le vitrage en place, avec des risques d'abrasion (essuie-glace, chiffon abrasif) et de contact avec des produits chimiques agressifs (polluants atmosphériques du type  $\text{SO}_2$ , produit d'entretien, ...).

Le choix s'est porté, en outre, sur un oxyde de titane qui soit au moins partiellement cristallisé parce qu'il a été montré qu'il était beaucoup plus performant en termes de propriété photo-catalytique que l'oxyde de titane amorphe. De préférence, il est cristallisé sous forme anatase, sous forme rutile ou sous forme d'un mélange d'anatase et de rutile, avec un taux de

cristallisation d'au moins 25%, notamment d'environ 30 à 80%, notamment près de la surface, (la propriété étant plutôt une propriété de surface). (On comprend par taux de cristallisation la quantité en poids de  $\text{TiO}_2$  cristallisé par rapport à la quantité en poids totale de  $\text{TiO}_2$  dans le revêtement).

On a également pu observer, notamment dans le cas d'une cristallisation sous forme anatase, que l'orientation des cristaux de  $\text{TiO}_2$  croissant sur le substrat avait une influence sur les performances photo-catalytiques de l'oxyde : il existe une orientation privilégiée (1,1,0) qui favorise nettement la photocatalyse.

Avantageusement, la fabrication du revêtement est opérée de manière à ce que l'oxyde de titane cristallisé qu'il contient se trouve sous forme de « cristallites », au moins près de la surface, c'est-à-dire de monocristaux, ayant une taille moyenne comprise entre 0,5 et 100 nm, de préférence 1 à 50 nm, notamment 10 à 40 nm, plus particulièrement entre 20 et 30 nm. C'est en effet dans cette gamme de dimension que l'oxyde de titane paraît avoir un effet photo-catalytique optimal, vraisemblablement parce que les cristallites de cette taille développent une surface active importante.

Comme on le verra plus en détail ultérieurement, on peut obtenir le revêtement à base d'oxyde de titane de multiples façons :

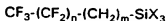
□ par décomposition de précurseurs de titane (techniques de pyrolyse : pyrolyse liquide, pyrolyse de poudre, pyrolyse en phase vapeur dite CVD (Chemical Vapor Deposition), techniques associées au sol-gel : trempé ou dipping, cell-coating, ...),

□ par une technique sous vide (pulvérisation cathodique réactive ou non).

Le revêtement peut comporter également, outre l'oxyde de titane cristallisé, au moins un autre type de matériau minéral, notamment sous forme d'un oxyde amorphe ou partiellement cristallisé, par exemple un oxyde de silicium (ou mélange d'oxydes), de titane, d'étain, de zirconium ou d'aluminium. Ce matériau minéral peut aussi participer à l'effet photocatalytique de l'oxyde de titane cristallisé, en présentant lui-même un certain effet photocatalytique, même faible par rapport à celui du  $\text{TiO}_2$  cristallisé, ce qui est le cas de l'oxyde d'étain ou de l'oxyde de titane amorphe.

Une couche d'oxyde « mixte » combinant ainsi de l'oxyde de titane au moins partiellement cristallisé à au moins un autre oxyde peut être intéressante sur le plan optique, tout particulièrement si l'autre ou les autres oxydes sont choisis d'indice inférieur à celui du  $\text{TiO}_2$  : en abaissant l'indice de réfraction « global » du revêtement, on peut jouer sur la réflexion lumineuse du substrat muni du revêtement, notamment abaisser cette réflexion. C'est le cas si, par exemple, on choisit une couche en  $\text{TiO}_2/\text{Al}_2\text{O}_3$ , dont un mode d'obtention est décrit dans le brevet EP-O 465 309, ou en  $\text{TiO}_2/\text{SiO}_2$ . Il est nécessaire, bien sûr, que le revêtement contienne cependant une teneur en  $\text{TiO}_2$  suffisante pour conserver une activité photocatalytique notable. On considère, ainsi, qu'il est préférable que le revêtement contienne au moins 40% en poids, notamment au moins 50% en poids de  $\text{TiO}_2$  par rapport au poids total d'oxyde(s) dans le revêtement.

On peut aussi choisir de superposer au revêtement selon l'invention une couche oléophobe et/ou hydrophobe greffée stable ou résistant à la photocatalyse, par exemple à base de l'organo-silane fluoré décrit dans les brevets US-5 368 892 et US-5 389 427, ainsi que du perfluoroalkylsilane décrit dans la demande de brevet FR-94/08734 du 13 juillet 1994 publiée sous le numéro FR-2 722 493 et correspondant au brevet européen EP-O 692 463, notamment de formule :



dans laquelle n est de 0 à 12, m est de 2 à 5 et X est un groupe hydrolysable.

Pour amplifier l'effet photocatalytique de l'oxyde de titane du revêtement selon l'invention, on peut tout d'abord augmenter la bande d'absorption du revêtement, en incorporant au revêtement d'autres particules notamment métalliques et à base de cadmium, d'étain, de tungstène, de zinc, de cérium, ou de zirconium.

On peut aussi augmenter le nombre de porteurs de charge par dopage du réseau cristallin de l'oxyde de titane, en y insérant au moins un des éléments métalliques suivants : niobium, tantale, fer, bismuth, cobalt, nickel, cuivre, ruthénium, cérium, molybdène.

Ce dopage peut aussi se faire par un dopage de surface seulement de l'oxyde de titane ou de l'ensemble du revêtement, dopage de surface réalisé

en recouvrant au moins une partie du revêtement d'une couche d'oxydes ou de sels métalliques, le métal étant choisi parmi le fer, le cuivre, le ruthénium, le cérium, le molybdène, le vanadium et le bismuth.

Enfin, on peut amplifier le phénomène photocatalytique en augmentant le rendement et/ou la cinétique des réactions photocatalytiques, en recouvrant l'oxyde de titane, ou au moins une partie du revêtement qui l'incorpore, par un métal noble sous forme de couche mince du type platine, rhodium, argent, palladium.

Un tel catalyseur, par exemple déposé par une technique sous vide, permet en fait d'augmenter le nombre et/ou la durée de vie des entités radicalaires créées par l'oxyde de titane, et ainsi de favoriser les réactions en chaîne conduisant à la dégradation de produits organiques.

De manière tout-à-fait surprenante, le revêtement présente en fait non pas une propriété mais deux, dès qu'il est exposé à un rayonnement adéquat comme dans le domaine du visible et/ou les ultraviolets, tel qu'un rayonnement solaire : par la présence d'oxyde de titane photocatalytique, comme déjà vu, il favorise la disparition progressive, au fur et à mesure de leur accumulation, de salissures d'origine organique, en provoquant leur dégradation par un processus d'oxydation radicalaire. Les salissures minérales ne sont, elles, pas dégradées par ce processus : elles restent donc sur la surface, et, à part certaines cristallisations, elles sont en partie facilement évacuées puisqu'elles n'ont plus de raison d'adhérer à la surface, les agents organiques collants étant dégradés par photocatalyse.

Mais le revêtement de l'invention, s'auto-nettoyant en permanence, présente également de préférence une surface extérieure à caractère hydrophile et/ou oléophile prononcé, ce qui induit trois effets très avantageux :

□ un caractère hydrophile permet un mouillage parfait de l'eau qui peut se déposer sur le revêtement. Quand un phénomène de condensation de l'eau se produit, au lieu d'un dépôt de gouttelettes d'eau sous forme de buée gênant la visibilité, on a en fait un mince film continu d'eau qui se forme à la surface du revêtement et qui est tout-à-fait transparent. Cet effet « anti-buée » est notamment démontré par la mesure d'un angle de contact à l'eau inférieur à 5° après exposition à la lumière, et,

☐ après ruissellement d'eau, de pluie notamment, sur une surface non traitée par une couche photocatalytique, de nombreuses gouttes d'eau de pluie restent accrochées sur la surface et laissent, une fois évaporées, des traces inesthétiques et gênantes, d'origine principalement minérale. En effet, une surface exposée à l'air ambiant se recouvre rapidement d'une couche de salissure qui limite son mouillage par l'eau. Ces salissures viennent s'ajouter aux autres salissures, notamment minérales (cristallisations, ...) apportées par l'atmosphère dans laquelle baigne le vitrage. Dans le cas d'une surface photoréactive, ces salissures minérales ne sont pas directement dégradées par photocatalyse. En fait, elles sont en très grande partie éliminées grâce au caractère hydrophile induit par l'activité photocatalytique. Ce caractère hydrophile provoque en effet un étalement parfait des gouttes de pluie. Les traces d'évaporation ne sont donc plus présentes. De plus, les autres salissures minérales présentes sur la surface sont lavées, ou redissoutes dans le cas de cristallisation, par le film d'eau et donc en grande partie évacuées. On obtient un effet « anti-salissure minérale » notamment induit par la pluie,

☐ conjointement à un caractère hydrophile, le revêtement peut aussi présenter un caractère oléophile, permettant le « mouillage » des salissures organiques qui, comme pour l'eau, tendent alors à se déposer sur le revêtement sous forme d'un film continu moins visible que des « taches » bien localisées. On obtient ainsi un effet « anti-salissures organiques » qui s'opère en deux temps : dès qu'elle se dépose sur le revêtement, la salissure est déjà peu visible. Ensuite, progressivement, elle disparaît par dégradation radicalaire amorcée par photo-catalyse.

Le revêtement peut être choisi de surface plus ou moins lisse. Une certaine rugosité peut en effet être avantageuse :

☐ elle permet de développer une surface photocatalytique active plus grande et donc elle induit une plus grande activité photocatalytique,

☐ elle a une influence directe sur le mouillage. La rugosité exalte en effet les propriétés de mouillage. Une surface lisse hydrophile sera encore plus hydrophile une fois rendue rugueuse. On comprend par « rugosité », ici, aussi bien la rugosité de surface, que la rugosité induite par une porosité de la couche dans au moins une partie de son épaisseur.

Les effets précédents seront d'autant plus marqués que le revêtement est poreux et rugueux, d'où un effet superhydrophile des surfaces photoréactives rugueuses. Cependant, trop prononcée, la rugosité peut être pénalisante en favorisant l'incrustation, l'accumulation des salissures et/ou en faisant apparaître un niveau de flou inacceptable optiquement.

Il s'est ainsi avéré intéressant d'adapter le mode de dépôt des revêtements à base de  $\text{TiO}_2$  de manière à ce qu'ils présentent une rugosité d'environ 2 à 20 nm, de préférence de 5 à 15 nm, cette rugosité étant évaluée par microscopie à force atomique, par mesure de la valeur de l'écart quadratique moyen (dit « Root Mean Square ou RMS en anglais) sur une surface de 1 micromètre carré. Avec de telles rugosités, les revêtements présentent un caractère hydrophile se traduisant par un angle de contact à l'eau pouvant être inférieur à  $1^\circ$ . On a également constaté qu'il était avantageux de favoriser une certaine porosité dans l'épaisseur du revêtement. Ainsi, si le revêtement n'est constitué que de  $\text{TiO}_2$ , il présente de préférence une porosité de l'ordre de 65 à 99%, notamment de 70 à 90%, la porosité étant définie ici de manière indirecte par le pourcentage de la densité théorique du  $\text{TiO}_2$ , qui est d'environ 3,8. Pour favoriser une telle porosité, un moyen consiste, par exemple, à déposer le revêtement par une technique du type sol-gel, impliquant la décomposition de matériaux de type organo-métalliques : on peut alors introduire dans la solution, outre le ou les précurseur(s) organo-métallique(s), un polymère organique du type polyéthylène glycol PEG : en durcissant la couche par chauffage, on brûle le PEG, ce qui engendre ou amplifie une certaine porosité dans l'épaisseur de la couche.

L'épaisseur du revêtement selon l'invention est variable, elle est de préférence comprise entre 5 nm et 1 micron, notamment entre 5 et 100 nm, notamment entre 10 et 80 nm, ou entre 20 et 50 nm. En fait, le choix de l'épaisseur peut dépendre de différents paramètres, notamment de l'application envisagée du substrat du type vitrage, ou encore de la taille des cristallites de  $\text{TiO}_2$  dans le revêtement ou de la présence d'alcalins en forte proportion dans le substrat.

Entre le substrat et le revêtement selon l'invention, on peut disposer une ou plusieurs autres couches minces à fonction différente ou complémentaire



de celle du revêtement. Il peut s'agir, notamment, de couches à fonction anti-statique, thermique, optique, ou favorisant la croissance cristalline de  $\text{TiO}_2$  sous forme anatase ou rutile, ou de couches faisant barrière à la migration de certains éléments provenant du substrat, notamment faisant barrière aux alcalins et tout particulièrement aux ions sodium quand le substrat est en verre.

On peut aussi envisager un empilement de couches « anti-reflets » alternant des couches minces à haut et bas indices, le revêtement selon l'invention constituant la dernière couche de l'empilement. Dans ce cas, il est préférable que le revêtement soit d'indice de réfraction relativement peu élevé, ce qui est le cas quand il est constitué d'un oxyde mixte de titane et de silicium.

La couche à fonction anti-statique et ou thermique (chauffante en la munissant d'amenées de courant, bas-émissive, anti-solaire, ...) peut notamment être choisie à base d'un matériau conducteur du type métal, comme l'argent, ou du type oxyde métallique dopé comme l'oxyde d'indium dopé à l'étain  $\text{ITO}$ , l'oxyde d'étain dopé avec un halogène du type fluor  $\text{SnO}_2\text{:F}$ , ou avec de l'antimoine  $\text{SnO}_2\text{:Sb}$ , ou de l'oxyde de zinc dopé à l'indium  $\text{ZnO:In}$ , au fluor  $\text{ZnO:F}$ , à l'aluminium  $\text{ZnO:Al}$  ou à l'étain  $\text{ZnO:Sn}$ . Il peut aussi s'agir d'oxydes métalliques sous-stoechiométriques en oxygène, comme  $\text{SnO}_{2-x}$  ou  $\text{ZnO}_{2-x}$  avec  $x < 2$ .

La couche à fonction anti-statique a de préférence une valeur de résistance carrée de 20 à 1000 ohms/carré. On peut prévoir de la munir d'amenées de courant afin de la polariser (tensions d'alimentation par exemple comprises entre 5 et 100V). Cette polarisation contrôlée permet notamment de lutter contre le dépôt de poussières de taille de l'ordre du millimètre susceptibles de se déposer sur le revêtement, notamment des poussières sèches adhérentes que par effet électro-statique : en inversant brutalement la polarisation de la couche, on « éjecte » ces poussières.

La couche mince à fonction optique peut être choisie afin de diminuer la réflexion lumineuse et/ou rendre plus neutre la couleur en réflexion du substrat. Elle présente dans ce cas, de préférence, un indice de réfraction intermédiaire entre celui du revêtement et celui du substrat et une épaisseur

optique appropriée, et peut être constituée d'un oxyde ou d'un mélange d'oxydes du type oxyde d'aluminium  $\text{Al}_2\text{O}_3$ , oxyde d'étain  $\text{SnO}_2$ , oxyde d'indium  $\text{In}_2\text{O}_3$ , oxycarbure ou oxynitride de silicium. Pour obtenir une atténuation maximale de la couleur en réflexion, il est préférable que cette couche mince présente un indice de réfraction proche de la racine carrée du produit des carrés des indices de réfraction des deux matériaux qui l'encadrent, c'est-à-dire le substrat et le revêtement selon l'invention. Parallèlement, il est avantageux de choisir son épaisseur optique (c'est-à-dire le produit de son épaisseur géométrique et de son indice de réfraction) voisine de  $\lambda/4$ ,  $\lambda$  étant approximativement la longueur d'onde moyenne dans le visible, notamment d'environ 500 à 550 nm.

La couche mince à fonction de barrière aux alcalins peut être notamment choisie à base d'oxyde, de nitrure, d'oxynitride ou d'oxycarbure de silicium, en oxyde d'aluminium contenant du fluor  $\text{Al}_2\text{O}_3:\text{F}$ , ou encore en nitrure d'aluminium. En fait, elle s'est avérée utile quand le substrat est en verre, car la migration d'ions sodium dans le revêtement selon l'invention peut, dans certaines conditions, en altérer les propriétés photocatalytiques.

La nature du substrat ou de la sous-couche a en outre un intérêt supplémentaire : elle peut favoriser la cristallisation de la couche photocatalytique que l'on dépose, notamment dans le cas du dépôt CVD.

Ainsi, lors de dépôt par CVD de  $\text{TiO}_2$ , une sous-couche de  $\text{SnO}_2:\text{F}$  cristallisée favorise la croissance de  $\text{TiO}_2$  sous forme majoritairement rutile, notamment pour des températures de dépôt de l'ordre de 400° à 500°C, alors que la surface d'un verre sodo-calcique ou d'une sous-couche d'oxycarbure de silicium induit plutôt une croissance anatase, notamment pour des températures de dépôt de l'ordre de 400° à 600°C.

Toutes ces couches minces optionnelles peuvent, de manière connue, être déposées par des techniques sous vide du type pulvérisation cathodique ou par d'autres techniques du type décomposition thermique telles que les pyrolyses en phase solide, liquide ou gazeuse. Chacune des couches prémentionnées peut cumuler plusieurs fonctions, mais on peut aussi les superposer.

L'invention a également pour objet les vitrages « anti-salissures » (salissures organiques et/ou minérales) et/ou « anti-buée », qu'ils soient monolithiques, multiples isolants du type double-vitrage ou feuilletés, et qui incorporent les substrats revêtus précédemment décrits.

L'invention vise donc la fabrication de produits verriers, céramiques ou vitro-céramiques, et tout particulièrement la fabrication de vitrages « auto-nettoyants ». Ceux-ci peuvent avantageusement être des vitrages de bâtiment, comme des double-vitrages (on peut alors disposer le revêtement « côté extérieur » et/ou « côté intérieur », c'est-à-dire en face 1 et/ou en face 4). Cela s'avère tout particulièrement intéressant pour les vitrages peu accessibles au nettoyage et/ou qui ont besoin d'être nettoyés très fréquemment, comme des vitrages de toiture, des vitrages d'aéroports, ... Il peut aussi s'agir de vitrages pour véhicules où le maintien de la visibilité est un critère essentiel de sécurité. Ce revêtement peut ainsi être disposé sur des pare-brise, latéraux ou lunettes arrière de voiture, notamment sur la face des vitrages tournée vers l'intérieur de l'habitacle. Ce revêtement peut alors éviter la formation de buée, et/ou supprimer les traces de salissures du type trace de doigts, nicotine ou matériau organique du type plastifiant volatil relargué par le plastique habillant l'intérieur de l'habitacle, notamment celui du tableau de bord (relargage connu parfois sous le terme anglais de « fogging »). D'autres véhicules tels qu'avions ou trains peuvent aussi trouver intérêt à utiliser des vitrages munis du revêtement de l'invention.

Nombre d'autres applications sont possibles, notamment pour les verres d'aquarium, les vitrines de magasin, les serres, les vérandas, les verres utilisés dans l'ameublement intérieur ou le mobilier urbain, mais aussi les miroirs, les écrans de télévision, le domaine de la lunetterie ou tout matériau d'architecture du type matériau de façade, de bardage, de toiture tel que des tuiles, ...

L'invention permet ainsi de fonctionnaliser ces produits connus, en leur conférant des propriétés anti-ultraviolet, anti-salissure, bactéricide, anti-reflet, anti-statique, anti-microorganisme, ...

Une autre application intéressante du revêtement selon l'invention consiste à l'associer à un vitrage à absorption variable commandée électriquement du type vitrage électrochrome, vitrage à cristaux liquides

éventuellement avec colorant dichroïque, vitrage à système de particules suspendues, vitrage viologène... Tous ces vitrages étant constitués en général d'une pluralité de substrats transparents entre lesquels sont disposés les éléments « actifs », on peut alors avantageusement disposer le revêtement sur la face extérieure d'au moins un de ces substrats.

Notamment dans le cas d'un vitrage électrochrome, lorsque ce dernier est à l'état coloré, son absorption conduit à un certain échauffement en surface, ce qui, de fait, est susceptible d'accélérer la décomposition photocatalytique des substances carbonées se déposant sur le revêtement selon l'invention. Pour plus de détails sur la structure d'un vitrage électrochrome, on se reportera avantageusement à la demande de brevet EP-A-0 575 207 décrivant un double vitrage feuilleté électrochrome, le revêtement selon l'invention pouvant, de préférence, être disposé en face 1.

L'invention a également pour objet les différents procédés d'obtention du revêtement selon l'invention. On peut avoir recours à une technique de dépôt du type pyrolyse, intéressante car elle permet notamment le dépôt du revêtement en continu, directement sur le ruban de verre float, lorsqu'on utilise un substrat verrier.

La pyrolyse peut s'effectuer en phase solide, à partir de poudre(s) de précurseur(s) du type organo-métallique(s).

La pyrolyse peut s'effectuer en phase liquide, à partir d'une solution comprenant un précurseur organo-métallique de titane du type chélate de titane et/ou alcoolate de titane. On mélange de tels précurseurs à au moins un autre précurseur organo-métallique. Pour plus de détails sur la nature du précurseur de titane ou sur les conditions de dépôt, on se rapportera par exemple aux brevets FR-2 310 977 et EP-O 465 309.

La pyrolyse peut aussi s'effectuer en phase vapeur, technique que l'on désigne également sous le terme de CVD (Chemical Vapor Deposition), à partir d'au moins un précurseur de titane du type halogénure tel que  $TiCl_4$  ou alcoolate de titane du type tétraisopropylate de Ti,  $Ti(OiPr)_4$ . La cristallisation de la couche peut en outre être contrôlée par le type de sous-couche, comme évoqué précédemment.

On peut également déposer le revêtement par d'autres techniques, notamment par les techniques associées au « sol-gel ». Différents modes de dépôt sont possibles, comme le « trempé » aussi appelé « dip-coating » ou un dépôt à l'aide d'une cellule appelé « cell-coating ». Il peut aussi s'agir d'un mode de dépôt par « spray-coating » ou par enduction laminaire, cette dernière technique étant détaillée dans la demande de brevet WO-94/01598. Tous ces modes de dépôt utilisent en général une solution comprenant au moins un précurseur organo-métallique, notamment de titane du type alcoolate que l'on décompose thermiquement après enduction du substrat par la solution sur l'une de ses faces, ou sur ses deux faces.

Il peut être intéressant, par ailleurs, de déposer le revêtement, quelle que soit la technique de dépôt envisagée, non pas en une seule fois, mais par au moins deux étapes successives, ce qui paraît favoriser la cristallisation de l'oxyde de titane sur toute l'épaisseur du revêtement lorsqu'on le choisit relativement épais.

De même, il est avantageux de faire subir au revêtement à propriété photo-catalytique, après dépôt, un traitement thermique du type recuit. Un traitement thermique est indispensable pour une technique du type sol-gel ou enduction laminaire afin de décomposer le (s) précurseur(s) organo-métallique(s) en oxyde, une fois l'enduction du substrat effectuée et améliorer la résistance à l'abrasion, ce qui n'est pas le cas lorsqu'on utilise une technique de pyrolyse où le précurseur se décompose dès qu'il se trouve au contact du substrat. Dans le premier cas comme dans le second, cependant, un traitement thermique post-dépôt, une fois le  $\text{TiO}_2$  formé, améliore son taux de cristallisation. La température de traitement choisie peut en outre permettre de mieux contrôler le taux de cristallisation et la nature cristalline, anatase et/ou rutile, de l'oxyde.

Cependant, dans le cas d'un substrat de verre sodo-calcique, des recuits multiples et prolongés peuvent favoriser une atténuation de l'activité photocatalytique à cause d'une trop grande migration des alcalins du substrat vers la couche photoréactive. L'utilisation d'une couche barrière entre le substrat, s'il est en verre standard, et le revêtement, ou le choix d'un substrat de verre de composition adéquate, ou encore le choix d'un verre

sodo-calcique dont la surface est désalcalinisée, permettent de s'affranchir de ce risque.

D'autres détails et caractéristiques avantageuses de l'invention ressortent de la description ci-après d'exemples de réalisation non limitatifs, à l'aide des figures suivantes :

- **figure 1** : une coupe transversale d'un substrat verrier muni du revêtement selon l'invention,
- **figure 2** : un schéma d'une technique de dépôt sol-gel, dite « par trempé » ou par « dip-coating » du revêtement,
- **figure 3** : un schéma d'une technique de dépôt dite « cell-coating »,
- **figure 4** : un schéma d'une technique de dépôt dite « spray-coating »,
- **figure 5** : un schéma d'une technique de dépôt par enduction laminaire.

Comme représenté de manière extrêmement schématique en figure 1, tous les exemples suivants concernent le dépôt d'un revêtement 3 dit « anti-salissures » essentiellement à base d'oxyde de titane sur un substrat transparent 1.

Le substrat 1 est en verre clair silico-sodo-calcique de 4 mm d'épaisseur et 50 cm de long et de large. Il va de soi que l'invention n'est pas limitée à ce type spécifique de verre. Le verre peut en outre ne pas être plan, mais bombé.

Entre le revêtement 3 et substrat 1, se trouve une couche mince optionnelle 2 soit à base d'oxycarbure de silicium noté SiOC en vue de constituer une barrière à la diffusion aux alcalins et/ou une couche atténuant la réflexion lumineuse, soit à base d'oxyde d'étain dopé au fluor  $\text{SnO}_2:\text{F}$  en vue de constituer une couche anti-statique et/ou bas-émissive, même à effet bas-émissif peu accentué, et/ou atténuant la couleur notamment en réflexion.

### **EXEMPLES 1 A 3**

Les exemples 1 à 3 concernent un revêtement 3 déposé à l'aide d'une technique de pyrolyse en phase liquide. On peut procéder en continu, en utilisant une buse de distribution adaptée disposée transversalement et au-dessus du ruban de verre float, au sortir de l'enceinte du bain float proprement dit. Ici, on a procédé de façon discontinue, en utilisant une buse mobile disposée face au substrat 1 déjà découpé aux dimensions indiquées, substrat qui est d'abord chauffé dans un four à une température de 400 à

650°C avant de défiler à vitesse constante devant la buse projetant une solution appropriée.

#### EXEMPLE 1

Dans cet exemple, il n'y a pas de couche optionnelle 2. Le revêtement 3 est déposé à l'aide d'une solution comprenant deux précurseurs organo-métalliques de titane, le di-iso-propoxy di-acétylacétonate de titane et le tétra-octylène glycolate de titane dissous dans un mélange de deux solvants, qui sont de l'acétate d'éthyle et de l'isopropanol.

On peut noter que d'autres précurseurs de même type sont tout-à-fait utilisables également, notamment d'autres chélates de titane du type acétylacétonate de titane, méthylacétoacétate de titane, éthylacétoacétate de titane ou encore le titane tri-éthanol amine ou le titane di-éthanol amine.

Dès que le substrat 1 a atteint la température voulue dans le four, soit notamment environ 500°C, celui-ci défile devant la buse projetant à température ambiante le mélange indiqué à l'aide d'air comprimé.

On obtient alors une couche de  $\text{TiO}_2$  d'environ 90 nm d'épaisseur, l'épaisseur pouvant être contrôlée par la vitesse de défilement du substrat 1 devant la buse et/ou la température dudit substrat. La couche est partiellement cristallisée sous forme anatase.

Cette couche présente une excellente tenue mécanique. Sa résistance aux tests d'abrasion est comparable à celle obtenue pour la surface du verre nu.

Elle est bombable et trempable. Elle ne présente pas de voile : la transmission lumineuse diffuse du substrat revêtu est inférieure à 0.6% (mesurée selon l'illuminant  $D_{65}$  à 560 nm).

#### EXEMPLE 2

Il renouvelle l'exemple 1, mais en intercalant entre le substrat 1 et revêtement 3 une couche 2 en  $\text{SnO}_2\cdot\text{F}$  de 73 nm d'épaisseur. Cette couche est obtenue par pyrolyse de poudre à partir de difluorure de dibutylétain DBTF. On peut aussi l'obtenir, de manière connue, par pyrolyse en phase liquide ou vapeur, comme cela est par exemple décrit dans la demande de brevet EP-A-O 648 196. En phase vapeur, on peut notamment utiliser un mélange de mono-

butyl trichlorure d'étain et d'un précurseur fluoré associé éventuellement à un oxydant « doux » du type  $H_2O$ .

L'indice de la couche obtenue est d'environ 1,9. Sa résistance carrée est d'environ 50 ohms.

Dans l'exemple 1 précédent, le substrat 1 revêtu, monté en double-vitrage de manière à ce que le revêtement soit en face 1 (avec un autre substrat 1' non revêtu mais de même nature et dimensions que le substrat 1 par l'intermédiaire d'une lame d'air de 12 mm) présente une valeur de pureté de couleur en réflexion de 26% et une valeur de pureté de couleur en transmission de 6,8%.

Dans cet exemple 2, la pureté de couleur en réflexion (dans les dorés) n'est plus que de 3,6%, et elle est de 1,1% en transmission.

Ainsi, la sous-couche en  $SnO_2:F$  permet de conférer au substrat des propriétés anti-statiques dues à sa conductivité électrique, elle a également une influence favorable sur la colorimétrie du substrat, en rendant nettement plus « neutre » sa coloration, aussi bien en transmission qu'en réflexion, coloration provoquée par la présence du revêtement 3 d'oxyde de titane présentant un indice de réfraction relativement élevé. On peut la polariser en la munissant d'une alimentation électrique adaptée, pour limiter le dépôt de poussières de taille relativement importante de l'ordre du millimètre.

En outre, cette sous-couche diminue la diffusion des alcalins dans la couche photocatalytique de  $TiO_2$ . L'activité photocatalytique est donc améliorée.

### EXEMPLE 3

Il renouvelle l'exemple 2, mais en intercalant cette fois entre substrat 1 et revêtement 3 une couche 2 à base d'oxycarbure de silicium, d'indice d'environ 1,75 et d'épaisseur environ 50 nm, couche que l'on peut obtenir par CVD à partir d'un mélange de  $SiH_4$  et d'éthylène en dilution dans de l'azote, comme décrit dans la demande de brevet EP-A-O 518 755. Cette couche est particulièrement efficace pour empêcher la tendance à la diffusion d'alcalins ( $Na^+$ ,  $K^+$ ) et d'alcalino-terreux ( $Ca^{++}$ ) provenant du substrat 1 vers le revêtement 3 et donc l'activité photocatalytique est nettement améliorée. Ayant, comme  $SnO_2:F$ , un indice de réfraction intermédiaire entre celui du



substrat (1,52) et du revêtement 3 (environ 2,30 à 2,35 ), elle permet également d'atténuer l'intensité de la coloration du substrat aussi bien en réflexion qu'en transmission et de diminuer globalement la valeur de réflexion lumineuse  $R_L$  dudit substrat.

Les exemples 4 à 7 suivants concernent des dépôts par CVD.

#### **EXEMPLE 4 A 7**

##### **EXEMPLE 4**

Cet exemple concerne le dépôt par CVD du revêtement 3 directement sur le substrat 1, à l'aide d'une buse standard comme celle représentée dans la demande de brevet EP-A-O 518 755 précitée. Comme précurseurs, on utilise soit un organo-métallique, soit un halogénure métallique. Ici on choisit comme organo-métallique le tétra-isopropylate de titane, intéressant pour sa grande volatilité et sa grande plage de températures d'utilisation, de 300 à 650°C. Le dépôt s'effectue dans cet exemple à environ 425°C, l'épaisseur de  $TiO_2$  est de 15 nm.

Le tétra-éthoxy titane  $Ti(O-Et)_4$  peut aussi convenir, et comme halogénure, on peut citer  $TiCl_4$ .

##### **EXEMPLE 5**

Il s'effectue similairement à l'exemple 4, sauf qu'ici on dépose la couche de 15 nm de  $TiO_2$  non pas directement sur le verre, mais sur une sous-couche en SiOC de 50 nm déposée comme dans l'exemple 3.

##### **EXEMPLE 6**

Il s'effectue comme l'exemple 4, sauf qu'ici l'épaisseur de la couche de  $TiO_2$  est de 65 nm.

##### **EXEMPLE 7**

Il s'effectue comme à l'exemple 5, sauf qu'ici l'épaisseur de la couche de  $TiO_2$  est de 60 nm.

De ces exemples 4 à 7, on constate que les substrats ainsi revêtus présentent une bonne tenue mécanique aux tests d'abrasion. En particulier, on n'observe pas de délamination de la couche de  $TiO_2$ .

##### **EXEMPLE 8**

Cet exemple utilise une technique associée au sol-gel utilisant un mode de dépôt par « trempé » encore appelé « dip-coating » dont le principe ressort

de la figure 2: il s'agit d'immerger le substrat 1 dans la solution liquide 4 contenant le(s) précurseur(s) adéquat(s) du revêtement 3, puis d'en extraire le substrat 1 à vitesse contrôlée à l'aide d'un moyen moteur 5, le choix de la vitesse d'extraction permettant d'ajuster l'épaisseur de solution restant à la surface des deux faces du substrat et, de fait, l'épaisseur des revêtements déposés, après traitement thermique de ce dernier pour à la fois évaporer le solvant et décomposer le ou les précurseurs en oxyde.

On utilise pour déposer le revêtement 3 une solution 4 comprenant soit du tétrabutoxyde de titane  $\text{Ti}(\text{O}-\text{Bu})_4$  stabilisé avec de la diéthanol amine DEA en proportion molaire 1:1 dans un solvant type éthanol à 0,2 mole de tétrabutoxyde par litre d'éthanol, soit le mélange de précurseurs et de solvants décrits dans l'exemple 1. ( Peut aussi être utilisé un autre précurseur comme le dibutoxy-diéthanolamine de titane).

Les substrats 1 peuvent comporter des sous-couches  $\text{SiOC}$ .

Après extraction de chacune des solutions 4, les substrats 1 sont chauffés 1 heure à  $100^\circ\text{C}$  puis environ 3 heures à  $550^\circ\text{C}$  avec une montée en température progressive.

On obtient sur chacune des faces un revêtement 3, dans les deux cas en  $\text{TiO}_2$  bien cristallisé sous forme anatase.

#### EXEMPLE 9

Cet exemple utilise la technique appelée « cell-coating » dont le principe est rappelé dans la figure 3. Il s'agit de former une cavité étroite délimitée par deux faces sensiblement parallèles 6, 7 et deux joints 8, 9, au moins une de ces faces 6, 7 étant constituée par la face du substrat 1 à traiter. Puis on remplit la cavité de la solution 4 de précurseur(s) du revêtement, et on retire la solution 4 de manière contrôlée, de manière à former un ménisque de mouillage à l'aide d'une pompe 10 péristaltique par exemple, en laissant un film de la solution 4 sur la face du substrat 1 au fur et à mesure du retrait de la solution.

La cavité 5 est ensuite maintenue au moins le temps nécessaire à un séchage. Le durcissement du film est effectué par traitement thermique. L'avantage de cette technique par rapport au « dip-coating » est notamment

que l'on peut traiter qu'une seule des deux faces du substrat 1, et non les deux systématiquement, à moins d'avoir recours à un système de masquage.

Les substrats 1 comportent des couches minces 2 à base d'oxycarbure de silicium SiOC.

L'exemple 6 utilise respectivement les solutions 4 décrites dans l'exemple 8. Les mêmes traitements thermiques sont ensuite opérés pour obtenir le revêtement 3 de  $TiO_2$ .

Le revêtement 3 présente une bonne durabilité mécanique.

Il apparaît au MEB (microscope électronique à balayage) un effet de champ sous la forme de « grains » de monocristaux de diamètre environ 30 nm. La rugosité de ce revêtement induit des propriétés de mouillage exaltées par rapport à un revêtement non rugueux.

Ces mêmes solutions 4 peuvent être également utilisées pour déposer des revêtements par « spray-coating », comme représenté en figure 4, où l'on pulvérise la solution 4 sous forme d'un nuage contre le substrat 1 en statique, ou par enduction laminaire comme représenté en figure 5. Dans ce dernier cas, on fait passer le substrat 1, maintenu par succion sous vide, contre un support 11 en inox et Téflon au-dessus d'un réservoir 12 contenant la solution, solution dans laquelle est partiellement immergé un cylindre 14 fendu, on déplace ensuite l'ensemble du réservoir 12 et du cylindre 14 sur toute la longueur du substrat 1, le masque 13 évitant une évaporation trop rapide du solvant de la solution 4. Pour plus de détails sur cette dernière technique, on se reportera avantageusement à la demande de brevet WO-94/01598 précitée.

Des tests ont été effectués sur les substrats obtenus selon les exemples précédents afin de caractériser les revêtements déposés et évaluer leurs performances « anti-buée » et « anti-salissures ».

□ Test 1 : c'est le test des figures de buée. Il consiste à observer les conséquences de la photo-catalyse et de la structure du revêtement (taux de groupes hydroxyl, porosité, rugosité) sur le mouillage. Si la surface est photo-réactive, les micro-pollutions carbonées qui se déposent sur le revêtement sont détruites en permanence, et la surface est hydrophile donc anti-buée. On peut aussi faire une évaluation quantitative en réchauffant

brusquement le substrat revêtu initialement, entreposé au froid ou simplement en soufflant sur le substrat, en mesurant s'il apparaît de la buée et dans l'affirmative, à quel moment, puis en mesurant le temps nécessaire à la disparition de ladite buée.

□ **Test 2** : il s'agit d'évaluer l'hydrophilie et l'oléophilie à la surface du revêtement 3, en comparaison de celles de la surface d'un verre nu, par la mesure d'angles de contact d'une goutte d'eau et d'une goutte de DOP (dioctyl-phthalate) à leurs surfaces, après avoir laissé les substrats une semaine à l'atmosphère ambiante sous éclairage naturel, dans le noir puis les avoir soumis 20 minutes à un rayonnement UVA.

□ **Test 3** : il consiste à déposer sur le substrat à évaluer une couche d'un organosilane et à l'irradier par des U.V.A. de manière à la dégrader par photocatalyse. L'organosilane modifiant les propriétés de mouillage, les mesures d'angle de contact à l'eau du substrat au cours de l'irradiation indiquent l'état de dégradation de la couche greffée. La vitesse de disparition de cette couche est reliée à l'activité photocatalytique du substrat.

L'organosilane greffé est un trichlorosilane : l'octadécyltrichlorosilane (OTS). Le greffage est réalisé par trempé.

L'appareil de test est constitué d'un carrousel tournant autour de 1 à 6 lampes U.V.A. basse pression. Les éprouvettes à évaluer sont placées dans le carrousel, la face à évaluer du côté du rayonnement U.V.A. Selon leur position et le nombre de lampes allumées, chaque éprouvette reçoit une irradiation U.V.A. variant de  $0,5 \text{ W/m}^2$  à  $50 \text{ W/m}^2$ . Pour les exemples 1, 2, 3, 8 et 9, la puissance d'irradiation est choisie de  $1,8 \text{ W/m}^2$ , et pour les exemples 4 à 7 de  $0,6 \text{ W/m}^2$ .

Le temps entre chaque mesure de l'angle de contact varie entre 20 min et 3 h, selon l'activité photocatalytique de l'éprouvette considérée. Les mesures sont effectuées à l'aide d'un goniomètre.

Avant irradiation, les verres présentent un angle d'environ  $100^\circ$ . On considère que la couche est détruite après irradiation lorsque l'angle est inférieur à  $20^\circ$ .

Chaque éprouvette testée est caractérisée par la vitesse moyenne de disparition de la couche, donnée en nanomètre par heure, c'est-à-dire

l'épaisseur de la couche d'organosilane déposée divisée, par la durée d'irradiation permettant d'atteindre un palier final inférieur à 20° (temps de disparition de la couche d'organosilane).

Tous les exemples précédents réussissent le test 1, c'est-à-dire que lorsqu'on souffle sur les substrats revêtus du revêtement, ils restent parfaitement transparents, alors que se dépose une couche de buée bien visible sur des substrats non revêtus.

Les exemples ont subi le test 2 : les substrats revêtus, après exposition aux rayonnements UVA, présentent un angle de contact à l'eau et au DOP d'au plus 5°. Au contraire, un verre nu dans les mêmes conditions présente un angle de contact à l'eau de 40° et un angle de contact au DOP de 20°.

Le tableau ci-dessous regroupe les résultats des substrats revêtus selon les exemples précédents au test 3.

Substrat	Test 3 de mouillage à 1,8 W/m <sup>2</sup> U.V.A. (en nm/h)
Exemple 1 (TiO <sub>2</sub> sur verre nu)	0,03
Exemple 2 (TiO <sub>2</sub> sur SnO <sub>2</sub> :F)	0,1
Exemple 3 (TiO <sub>2</sub> sur SiOC)	0,2
Exemple 8 (TiO <sub>2</sub> sur 50 nm SiOC)	5
Exemple 9 (TiO <sub>2</sub> sur 50 nm SiOC)	5
Verre nu	0

Substrat (CVD)	Test 3 de mouillage à 0,6 W/m <sup>2</sup> U.V.A. (en nm/h)
Exemple 4 (TiO <sub>2</sub> sur verre nu)	< 0,05 nm/h
Exemple 5 (TiO <sub>2</sub> sur SiOC)	4
Exemple 6 (TiO <sub>2</sub> sur verre nu)	9
Exemple 7 (TiO <sub>2</sub> sur SiOC)	19,5

Du tableau, on peut constater que la présence de sous-couches, notamment en SiOC, favorise l'activité photocatalytique du revêtement

contenant le  $\text{TiO}_2$ , par son effet de barrière aux alcalins et alcalino-terreux pouvant migrer du verre (comparaison des exemples 4 et 5 ou 6 et 7).

On observe aussi que l'épaisseur du revêtement contenant le  $\text{TiO}_2$  joue également un rôle (comparaison des exemples 1 et 3) : pour une épaisseur de revêtement en  $\text{TiO}_2$  supérieure à la taille moyenne des mono-cristaux ou « cristallites », on obtient un meilleur effet photocatalytique.

En fait, on a pu observer que ce sont les revêtements en  $\text{TiO}_2$  obtenus par CVD qui présentent la cristallisation la plus poussée, avec des tailles de cristallites de l'ordre de 20 à 30 nm. On peut constater que l'activité photocatalytique de l'exemple 6 (65 nm de  $\text{TiO}_2$ ) est nettement supérieure à celle de l'exemple 4 (15 nm de  $\text{TiO}_2$  seulement). Il est donc avantageux de prévoir une épaisseur de revêtement de  $\text{TiO}_2$  au moins deux fois supérieure au diamètre moyen des cristallites qu'il contient. Alternativement, comme c'est le cas de l'exemple 5, on peut conserver une épaisseur mince de revêtement en  $\text{TiO}_2$  mais alors choisir d'utiliser une sous-couche de nature et d'épaisseur appropriées pour favoriser au mieux la croissance cristalline de  $\text{TiO}_2$  dès la « première » couche de cristallites.

On a pu observer que la cristallisation du  $\text{TiO}_2$  était un peu moins poussée pour les revêtements déposés par une autre technique que la CVD. Là encore, tout est cependant affaire de compromis : une cristallisation moins poussée et une activité photocatalytique a priori moins élevée peuvent être « compensées » par l'utilisation d'un procédé de dépôt moins onéreux ou moins complexe, par exemple. De plus, l'utilisation d'une sous-couche appropriée ou le dopage du  $\text{TiO}_2$  peuvent permettre d'améliorer les performances photocatalytiques si nécessaire.

On vérifie aussi de la comparaison des exemples 2 et 3 que la nature de la sous-couche influe sur le mode de cristallisation et, de fait, sur l'activité photocatalytique du revêtement.

**REVENDICATIONS**

1. Substrat (1) à base verrière, céramique ou vitro-céramique, muni sur au moins une partie d'au moins une de ses faces d'un revêtement (3) à propriété photo-catalytique comportant de l'oxyde de titane au moins partiellement cristallisé.
2. Substrat (1) selon la revendication 1, caractérisé en ce que l'oxyde de titane cristallisé est sous forme anatase, sous forme rutile ou sous forme d'un mélange d'anatase et de rutile.
3. Substrat (1) selon la revendication 1 ou la revendication 2, caractérisé en ce que l'oxyde de titane est cristallisé avec un taux de cristallisation d'au moins 25%, notamment compris entre 30 et 80%.
4. Substrat (1) selon l'une des revendications précédentes, caractérisé en ce que l'oxyde de titane cristallisé est sous forme de cristallites de taille moyenne comprise entre 0,5 et 60 nm, de préférence 1 à 50, notamment 10 à 40 nm.
5. Substrat (1) selon l'une des revendications précédentes, caractérisé en ce que le revêtement (3) comporte également un matériau minéral, notamment sous forme d'un oxyde ou mélange d'oxydes amorphe ou partiellement cristallisé du type oxyde de silicium, oxyde de titane, oxyde d'étain, oxyde de zirconium, oxyde d'aluminium.
6. Substrat (1) selon l'une des revendications précédentes, caractérisé en ce que le revêtement comprend des additifs aptes à amplifier le phénomène photocatalytique dû à l'oxyde de titane, notamment en augmentant la bande d'absorption du revêtement et/ou en augmentant le nombre de porteurs de charges par dopage du réseau cristallin de l'oxyde ou par dopage de surface du revêtement et/ou en augmentant rendement et cinétique des réactions photocatalytiques en recouvrant au moins une partie du revêtement par un catalyseur.
7. Substrat (1) selon la revendication 6, caractérisé en ce que le réseau cristallin de l'oxyde de titane est dopé, notamment par au moins un des éléments métalliques du groupe comprenant le niobium, le tantale, le fer, le bismuth, le cobalt, le nickel, le cuivre, le ruthénium, le cérium, le molybdène.

8. Substrat (1) selon la revendication 6, caractérisé en ce que l'oxyde de titane ou le revêtement (3) dans son ensemble est revêtu d'un catalyseur, notamment sous la forme de couche mince de métal noble du type platine, rhodium, argent, palladium.

9. Substrat (1) selon la revendication 6, caractérisé en ce que le revêtement incorpore des éléments métalliques, notamment sous forme de particules, visant à augmenter sa bande d'absorption, éléments choisis parmi l'étain, le cadmium, le tungstène, le cérium ou le zirconium.

10. Substrat (1) selon la revendication 6, caractérisé en ce que le dopage de surface de l'oxyde de titane ou du revêtement qui le comporte est réalisé en recouvrant au moins une partie dudit revêtement d'une couche d'oxyde ou de sels métalliques, le métal étant choisi parmi le fer, le cuivre, le ruthénium, le cérium, le molybdène, le bismuth, le vanadium.

11. Substrat (1) selon l'une des revendications précédentes, caractérisé en ce que la surface du revêtement (3) est hydrophile, avec notamment un angle de contact à l'eau inférieur à 5° après exposition à un rayonnement lumineux, et/ou oléophile.

12. Substrat (1) selon l'une des revendications précédentes, caractérisé en ce que l'épaisseur du revêtement (3) est compris entre 5 nm et 1 micron, notamment entre 5 et 100 nm, de préférence 10 à 80, notamment 20 à 50 nanomètres.

13. Substrat (1) selon l'une des revendications précédentes, caractérisé en ce que la rugosité RMS du revêtement (3) est comprise entre 2 et 20 nm, notamment entre 5 et 20 nm.

14. Substrat (1) selon l'une des revendications précédentes, caractérisé en ce qu'est disposée sous le revêtement (3) à propriété photocatalytique au moins une couche mince (2) à fonction anti-statique, thermique, optique, ou faisant barrière à la migration des alcalins provenant du substrat (1).

15. Substrat (1) selon la revendication 14, caractérisé en ce que la couche mince (2) à fonction anti-statique, éventuellement à polarisation contrôlée, et/ou thermique et/ou optique est à base de matériau conducteur du type métal ou du type oxyde métallique dopé tel que ITO,  $\text{SnO}_2\cdot\text{F}$ ,  $\text{ZnO}:\text{In}$ ,



$\text{ZnO:F}$ ,  $\text{ZnO:Al}$ ,  $\text{ZnO:Sn}$  ou oxyde métallique sous-stoechiométrique en oxygène comme  $\text{SnO}_{2-x}$  ou  $\text{ZnO}_{2-x}$  avec  $x < 2$ .

16. Substrat (1) selon la revendication 14, caractérisé en ce que la couche mince (2) à fonction optique est à base d'un oxyde ou d'un mélange d'oxydes dont l'indice de réfraction est intermédiaire entre celui du revêtement et celui du substrat, notamment choisi(s) parmi les oxydes suivants :  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ , oxycarbure ou oxynitride de silicium.

17. Substrat (1) selon la revendication 14, caractérisé en ce que la couche mince (2) à fonction de barrière aux alcalins est à base d'oxyde, de nitride, d'oxynitride ou d'oxycarbure de silicium, d' $\text{Al}_2\text{O}_3:\text{F}$  ou de nitride d'aluminium.

18. Substrat (1) selon la revendication 14, caractérisé en ce que le revêtement (3) constitue la dernière couche d'un empilement de couches anti-reflets.

19. Vitrage « anti-salissures et/ou anti-buée », monolithique, multiple du type double-vitrage ou feuilleté incorporant le substrat (1) selon l'une des revendications précédentes.

20. Application du substrat (1) selon l'une des revendications 1 à 18 à la fabrication de vitrages « auto-nettoyants », anti-buée et/ou anti-salissures, du type salissures organiques et/ou minérales, notamment des vitrages pour le bâtiment du type double-vitrage, des vitrages pour véhicules du type pare-brise, lunette arrière ou latéraux d'automobile, trains, avions, ou vitrages utilitaires comme des verres d'aquarium, de vitrines, de serre, d'ameublement intérieur, de mobilier urbain, ou des miroirs, écrans de télévision, vitrages à absorption variable commandée électriquement.

21. Procédé d'obtention du substrat (1) selon l'une des revendications 1 à 18, caractérisé en ce qu'on dépose le revêtement (3) à propriété photocatalytique par pyrolyse en phase liquide, notamment à partir d'une solution comprenant au moins un précurseur organo-métallique de titane du type chélate de titane et/ou alcoolate de titane.

22. Procédé d'obtention du substrat (1) selon l'une des revendications 1 à 18, caractérisé en ce qu'on dépose le revêtement (3) à propriété photocatalytique par une technique de sol-gel, avec un mode de dépôt du type

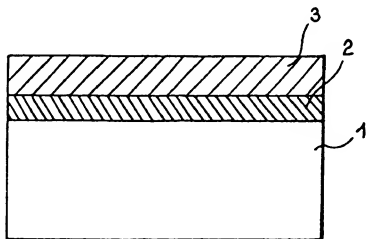
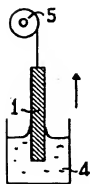
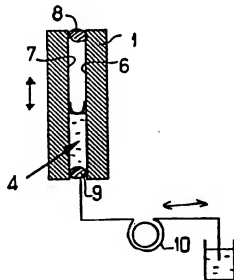
trempé ou dip-coating, cell-coating, spray-coating, ou enduction laminaire, à partir d'une solution comprenant au moins un précurseur organo-métallique de titane du type alcoolate de titane.

23. Procédé d'obtention du substrat (1) selon l'une des revendications 1 à 18, caractérisé en ce qu'on dépose le revêtement (3) à propriété photo-catalytique par pyrolyse en phase vapeur, CVD, à partir d'au moins un précurseur de titane du type halogénure ou organo-métallique.

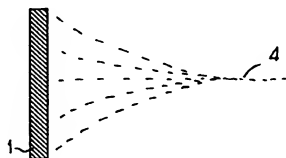
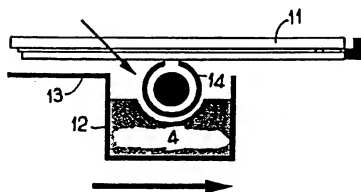
24. Procédé selon l'une des revendications 21 à 23, caractérisé en ce qu'on dépose le revêtement (3) à propriété photo-catalytique en au moins deux étapes successives.

25. Procédé selon l'une des revendications 21 à 24, caractérisé en ce qu'on fait subir au revêtement (3) à propriété photo-catalytique, après dépôt, au moins un traitement thermique du type recuit.

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FIG. 1FIG. 2FIG. 3

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FIG. 4FIG. 5

## INTERNATIONAL SEARCH REPORT

national Application No  
PCT/FR 96/01421

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C03C17/00 C03C8/20 C03C17/34

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 23 Derwent Publications Ltd., London, GB; AN 88-158890 XP002005574 & JP,A,63 100 042 (NIPPON SHEET GLASS KK) , 2 May 1988 see abstract ---	1-6,8, 11-25
X	JOURNAL OF MATERIALS SCIENCE, vol. 24, no. 1, January 1989, LONDON GB, pages 243-246, XP000046035 M.TAKAHASHI ET AL.: "pt-tio2 thin films on glass substrates as efficient photocatalysts" see the whole document ---	1-6,8, 11-25
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

International Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 544 577 (SAINT GOBAIN VITRAGE INTERNATIONAL) 2 June 1993 see claims 1-10	14-18
A	--- CHEMICAL ABSTRACTS, vol. 116, no. 10, 9 March 1992 Columbus, Ohio, US; abstract no. 89812a, page 396; XP000405429 see abstract & SU,A,1 663 046 (SCIENTIFIC RESEARCH INSTITUTE OF PHYSICAL CHEMICAL PROBLEMS MINSK) 15 July 1991 -----	1-10

## INTERNATIONAL SEARCH REPORT

Information on patent family members

National Application No

PCT/FR 96/01421

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-544577	02-06-93	FR-A- 2684095	28-05-93
		BR-A- 9204545	01-06-93
		CA-A- 2083671	27-05-93
		JP-A- 5229852	07-09-93
		US-A- 5342676	30-08-94
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# RAPPORT DE RECHERCHE INTERNATIONALE

1. sous Internationale No  
PCT/FR 96/01421

<b>A. CLASSEMENT DE L'OBJET DE LA DEMANDE</b> CIB 6 C03C17/00 C03C8/20 C03C17/34		
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Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si cela est réalisable, termes de recherche utilisés)		
<b>C. DOCUMENTS CONSIDERES COMME PERTINENTS</b>		
Catégorie *	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
X	DATABASE WPI Week 23 Derwent Publications Ltd., London, GB; AN 88-158890 XP002005574 & JP,A,63 100 042 (NIPPON SHEET GLASS KK) , 2 Mai 1988 voir abrégé	1-6,8, 11-25
X	--- JOURNAL OF MATERIALS SCIENCE, vol. 24, no. 1, Janvier 1989, LONDON GB, pages 243-246, XP000046035 M.TAKAHASHI ET AL.: "pt-tio2 thin films on glass substrates as efficient photocatalysts" voir le document en entier --- -/--	1-6,8, 11-25
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Nom et adresse postale de l'administration chargée de la recherche internationale Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tél. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Fonctionnaire autonome  Reedijk, A



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Catégorie	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
A	EP,A,0 544 577 (SAINT GOBAIN VITRAGE INTERNATIONAL) 2 Juin 1993 voir revendications 1-10 ---	14-18
A	CHEMICAL ABSTRACTS, vol. 116. no. 10, 9 Mars 1992 Columbus, Ohio, US; abstract no. 89812a, page 396; XP000405429 voir abrégé & SU,A,1 663 046 (SCIENTIFIC RESEARCH INSTITUTE OF PHYSICAL CHEMICAL PROBLEMS MINSK) 15 Juillet 1991 -----	1-10

Formulaire PCT/ISA/210 (suite de la deuxième feuille) (juillet 1992)

# RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres de familles de brevets

ande Internationale No

PCT/FR 96/01421

Document brevet cité au rapport de recherche	Date de publication	Membre(s) de la famille de brevets(s)	Date de publication
EP-A-544577	02-06-93	FR-A- 2684095	28-05-93
		BR-A- 9204545	01-06-93
		CA-A- 2083671	27-05-93
		JP-A- 5229852	07-09-93
		US-A- 5342676	30-08-94
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C03C 17/245, 17/25, 17/34</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/41480</b> <b>(43) International Publication Date:</b> 24 September 1998 (24.09.98)
<b>(21) International Application Number:</b> PCT/US98/04785 <b>(22) International Filing Date:</b> 12 March 1998 (12.03.98)  <b>(30) Priority Data:</b> 60/040,566              14 March 1997 (14.03.97)      US 08/899,257              23 July 1997 (23.07.97)      US  <b>(71) Applicant:</b> PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US).  <b>(72) Inventors:</b> GREENBERG, Charles, B.; 3268 Windgate Drive, Murrysville, PA 15668 (US). HARRIS, Caroline, S.; 921 Farragut Street, Pittsburgh, PA 15206 (US). KORTHUIS, Vincent; 6900 Aimpont Drive, Plano, TX 75023 (US). KUTILEK, Luke, A.; 528 Ninth Street, Oakmont, PA 15139 (US). SINGLETON, David, E.; 1535 Route 908, Natrona Heights, PA 15065 (US). SZANYI, Janos; 305 3rd Street, Oakmont, PA 15139 (US). THIEL, James, P.; Apartment 6A, 5523 Ellsworth, Pittsburgh, PA 15232 (US).  <b>(74) Agents:</b> LEPIANE, Donald, C.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PHOTOCATALYTICALLY-ACTIVATED SELF-CLEANING ARTICLE AND METHOD OF MAKING SAME		
<div data-bbox="220 726 759 813" data-label="Image"> </div> <p data-bbox="96 846 182 860"><b>(57) Abstract</b></p> <p data-bbox="96 876 939 964">A method and article are disclosed wherein a substrate is provided with a photocatalytically-activated self-cleaning surface by forming a photocatalytically-activated self-cleaning coating on the substrate by spray pyrolysis chemical vapor deposition or magnetron sputter vacuum deposition. The coating has a thickness of at least about 500 Angstroms to limit sodium-ion poisoning to a portion of the coating facing the substrate. Alternatively, a sodium ion diffusion barrier layer is deposited over the substrate prior to the deposition of the photocatalytically-activated self-cleaning coating to prevent sodium ion poisoning of the photocatalytically-activated self-cleaning coating. The substrate includes glass substrates, including glass sheet and continuous float glass ribbon.</p>		

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PHOTOCATALYTICALLY-ACTIVATED SELF-CLEANING ARTICLE  
AND METHOD OF MAKING SAME

CROSS REFERENCE TO RELATED APPLICATIONS

- 5           This application claims the benefit of U.S. Provisional Application Serial No. 60/040,566 filed March 14, 1997. U.S. Provisional Application Serial No. 60/040,565 filed March 14, 1997, and U.S. Regular Application No. \_\_\_\_\_ to Greenberg et al., entitled "Photocatalytically-  
10 Activated Self-Cleaning Appliances", filed even date herewith, are also related to the present application and are hereby incorporated by reference.

BACKGROUND OF THE INVENTION

15   Field of the Invention

- The present invention relates to a method of depositing a photocatalytically-activated self-cleaning coating on a substrate (e.g. glass sheet or a continuous glass, float ribbon), to a method of preventing sodium ion poisoning  
20 of the photocatalytically-activated self cleaning coating deposited over a sodium ion containing substrate and to articles of manufacture prepared according to the methods.

Description of the Related Art

- 25           For many substrates (e.g. glass substrates), it is desirable that the surface of the substrate remain "clean," that is to say free of surface contaminants, e.g. common organic and inorganic surface contaminants. Traditionally, this has meant that such surfaces must be cleaned frequently.  
30 This cleaning operation is typically performed manually or by mechanical devices. Either approach is quite labor, time and/or cost intensive. A need exists for substrates having

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surfaces that are self-cleaning or at least easier to clean, which would eliminate or reduce the need for such manual or mechanical cleaning.

- Titanium dioxide ( $\text{TiO}_2$ ) coatings are known to
- 5 provide a photocatalytically-activated self-cleaning (hereinafter "PASC") surface on a substrate. Publications directed to the formation of a PASC titanium dioxide coating on a glass substrate include U.S. Patent No. 5,595,813 and "Photooxidative Self-cleaning Transparent Titanium Dioxide
- 10 Films on Glass", Paz et al., J. Mater. Res., Vol. 10, No. 11, pp. 2842-48 (Nov. 1995). Further, a bibliography of patents and articles relating generally to the photocatalytic oxidation of organic compounds is reported in Bibliography of Work On The Photocatalytic Removal of Hazardous Compounds from
- 15 Water and Air, D. Blake, National Renewable Energy Laboratory (May 1994) and in an October 1995 update and an October 1996 update.

- A presently available method of applying a PASC coating (e.g. a titanium dioxide PASC coating) to a substrate
- 20 is the sol-gel method. With the sol-gel method an uncrystallized alcohol-solvent-based colloidal suspension (the sol) is spray, spin, or dip coated onto a substrate at or about room temperature. The substrate is then heated to a temperature within the range of about 100°C to 800°C (212°F to
- 25 1472°F), to either bond the PASC coating to the substrate and/or to cause the crystallization of the PASC coating, in order to form a crystallized PASC coating (the gel) on the substrate.

- One limitation of applying a sol-gel PASC coating is
- 30 that the sol-gel coating method is not economically or practically compatible with certain application conditions or substrates. For example, when it is desired to provide a PASC

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- coating on a float ribbon during manufacture thereof, the ribbon may be too hot to accept the sol depending in part, on the solvent used in the sol solution. For many solvents used in sol-gel process, it is required to cool the hot float
- 5 ribbon to about room temperature before applying the sol, and to reheat the float ribbon to a temperature sufficient to crystallize the sol into a PASC coating. Such cooling and reheating operations require a substantial investment in equipment, energy and handling costs, and significantly
- 10 decrease production efficiency.

- The PASC activity of PASC coatings may be significantly reduced or destroyed if sodium ions are present in the substrate and migrate from the substrate into the PASC coating. This process is known as sodium poisoning or sodium
- 15 ion poisoning. For many substrates which contain sodium ions, the rate of migration of sodium ions into coatings increases as the temperature of the substrate increases. Thus another limitation of the sol-gel coating method is that reheating the substrate increases the opportunity for sodium ion migration,
- 20 and in turn, sodium ion poisoning of a PASC coating.

- Another limitation of forming PASC coatings by the sol-gel method is the thickness of the coatings e.g. several microns thick. Such thick PASC coatings may have an adverse affect on the optical and/or aesthetic properties of PASC
- 25 coated articles.

- As can be appreciated from the foregoing, a need exists for an article of manufacture having a PASC coating deposited therein and for a method of depositing a PASC coating that does not suffer from the drawbacks known in the
- 30 art.

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SUMMARY OF THE INVENTION

The present invention is directed to a PASC article of manufacture which includes a substrate having at least one surface and a PASC coating, e.g. titanium dioxide, deposited  
5 over the surface of the substrate by a process selected from the group consisting of chemical vapor deposition (hereinafter "CVD"), spray pyrolysis and magnetron sputtered vacuum deposition (hereinafter "MSVD"). The present invention is also directed to a method of making such an article of  
10 manufacture.

The present invention is also directed to a PASC article of manufacture which includes a substrate having at least one surface, a sodium ion diffusion barrier (hereafter "SIDB") layer e.g. tin oxide, titanium dioxide, aluminum oxide  
15 layers and mixtures thereof deposited over the surface of the substrate, and a PASC coating e.g. a titanium dioxide coating deposited over the SIDB layer. The PASC coating and the SIDB layer are each deposited by a process selected from the group consisting of CVD, spray pyrolysis and MSVD. The present  
20 invention is also directed to a method of making such an article of manufacture.

DESCRIPTION OF THE DRAWINGS

Fig. 1 is an elevational view of a portion of a  
25 substrate having a PASC coating dispersed thereon.

Fig. 2 is a view similar to the view of Fig. 1 illustrating an SIDB layer interposed between the substrate and the PASC coating.

Fig. 3 is a schematic view of selected components of  
30 a CVD coater.

Fig. 4 is a schematic view of selected components of a spray pyrolysis coater.



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DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to Fig. 1, there is shown an article 20 having features of the present invention. The article 20 includes a substrate 22 having deposited thereon a PASC coating 24. The substrate 22 is not limiting to the invention and may include a glass substrate e.g. a glass sheet or a continuous glass float ribbon, a plastic substrate, a metal substrate and an enameled substrate.

The PASC coating 24 may be directly over the substrate 22 as shown in Figure 1 or in the alternative other layers may be interposed between the PASC coating 24 and the substrate 22, e.g. including but not limited to an SIBD layer 26 as shown in Figure 2 and as described in more detail hereafter. Further, as may be appreciated by those skilled in the art, the PASC coating 24 may be the uppermost layer of a multilayer stack of coatings present on substrate 22 or the PASC coating 24 may be embedded as one of the layers other than the uppermost layer within such a multi-layer stack provided sufficient actinic radiation may pass through any coatings deposited above PASC coating 24 to photocatalytically activate PASC coating 24 and provided active radicals can pass through the coatings deposited above the PASC coating 24 to react with the organic contaminants present on the uppermost layer of the multilayer stack.

The PASC coating 24 may be any coating which is photocatalytically activated to be self-cleaning and which can be deposited by the CVD method, the spray pyrolysis method or the MSVD method. For example but not limiting to the invention, the PASC coating 24 may include one or more metal oxides such as titanium oxides, iron oxides, silver oxides, copper oxides, tungsten oxides, zinc oxides, zinc/tin oxides,

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strontium titanate and mixtures thereof. The metal oxide may include oxides, super-oxides or sub-oxides of the metal.

A preferred PASC coating 24 is a titanium dioxide coating. Titanium dioxide exists in an amorphous form and  
5 three crystalline forms, namely the anatase, rutile and brookite crystalline forms. Anatase phase titanium dioxide, is preferred because it exhibits strong PASC activity while also possessing excellent resistance to chemical attack and excellent physical durability. Further, anatase phase  
10 titanium dioxide has high transmission in the visible region of the spectrum which gives thin coatings of anatase titanium dioxide with excellent optical properties. The rutile phase of titanium dioxide also exhibits PASC activity. Combinations of the anatase and/or rutile phases with the brookite and/or  
15 amorphous phases are acceptable for the present invention provided the combination exhibits PASC activity.

The PASC coating 24 must be sufficiently thick so as to provide an acceptable level of PASC activity. There is no absolute value which renders the PASC coating 24 "acceptable"  
20 or "unacceptable" because whether a PASC coating has an acceptable level of PASC activity is largely determined by the purpose and conditions under which the PASC coated article is being used and the performance standards selected in connection with that purpose. In general, thicker PASC  
25 coatings provide higher PASC activity. However, other considerations may weigh toward a thinner coating, e.g. thinner coatings are preferred when the article is to have high transmission for aesthetic or optical reasons; the surface contaminants on the surface of the article are easily  
30 removed with a thinner PASC coating, the coating is exposed to substantial irradiation and/or the PASC coating 24 will be exposed to sodium ion poisoning discussed in more detail

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- below. For a wide variety of applications, it is preferred that the PASC coating is at least about 200 Angstroms (Å), preferably at least about 400Å and more preferably at least about 500Å thick. It has been found that when the substrate
- 5 22 is a piece of float glass and the PASC coating 24 is an anatase titanium dioxide PASC coating formed directly over the piece of float glass by the CVD method, that a thickness of at least about 500Å provides a PASC reaction rate in the range of about  $2 \times 10^{-3}$  to about  $5 \times 10^{-3}$  per centimeter minute
- 10 (hereinafter " $\text{cm}^3\text{min}^{-1}$ ") for the removal of a stearic acid test film when the PASC coating was exposed to ultraviolet radiation from a light source such as that sold under the tradename UVA-340 by the Q-Panel Company of Cleveland, Ohio, having an intensity of about 20 watts per square meter
- 15 (hereinafter  $\text{W/m}^2$ ) at the PASC coating surface which is acceptable for a wide range of applications.

- In accordance with the present invention, a thin e.g., less than 1 micron, more preferably less than 0.5 micron PASC coating is formed on the substrate 22 by spray pyrolysis
- 20 CVD or MSVD methods. In the spray pyrolysis method a metal-containing precursor is carried either in an aqueous suspension, e.g. an aqueous solution, and in the CVD method a carrier gas, e.g. nitrogen gas, and directed toward the surface of the substrate 22 while the substrate 22 is at a
- 25 temperature high enough to cause the metal-containing precursor to decompose and to form a PASC coating 24 on the substrate 22. In the MSVD method, a metal-containing cathode target is sputtered under negative pressure in an inert or oxygen-containing atmosphere to deposit a sputter coating over
- 30 substrate 22. The substrate 22 during or after coating is heated to cause crystallization of the sputter coating to form the PASC coating 24.

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Each of the methods has advantages and limitations e.g. the CVD method and pyrolysis method are preferred over the spray pyrolysis method because the aqueous solution of the spray pyrolysis method may result in the presence of OH<sup>-</sup> ions in the PASC coating 24, which may, in turn, inhibit proper crystalline formation in the PASC coating 24 thereby reducing the PASC activity of the coating. The CVD method and pyrolysis method are preferred over the MSVD method because it is compatible with coating continuous substrates found at elevated temperatures e.g. glass float ribbons. The CVD, spray pyrolysis and MSVD methods of depositing PASC coating 24 are discussed in more detail below. As may be appreciated, spray pyrolysis and CVD methods may be used to deposit thin (e.g., a few hundred Angstrom thick) metal oxide coatings (including titanium dioxide coatings) over a substrate. Such coatings are described in U.S. Patent Nos. 4,344,986; 4,393,095; 4,400,412; 4,719,126; 4,853,257; and 4,971,843 which patents are hereby incorporated by reference.

Metal-containing precursors that may be used in the practice of the present invention to form titanium dioxide PASC coatings by the CVD method include but are not limited to titanium tetrachloride (TiCl<sub>4</sub>), titanium tetraisopropoxide (Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) (hereinafter "TTIP") and titanium tetraethoxide (Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) (hereinafter "TTET"). Carrier gases that may be used in the CVD method include but are not limited to air, nitrogen, oxygen, ammonia and mixtures thereof. The preferred carrier gas is nitrogen and the preferred metal-containing precursor is TTIP. The concentration of the metal-containing precursor in the carrier gas is generally in the range of 0.1% to 0.4% by volume for the three listed metal-containing precursors, but as may be appreciated by those skilled in the

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art, these concentrations may be varied for other metal-containing precursors.

Metal-containing precursors that may be used in the practice of the invention to form PASC coatings by the spray  
5 pyrolysis method include relatively water insoluble organometallic reactants, specifically metal acetylacetonate compounds, which are jet milled or wet ground to a particle size of less than about 10 microns and suspended in an aqueous medium by the use of a chemical wetting agent. A suitable  
10 metal acetylacetonate to form a titanium dioxide PASC coating is titanyl acetylacetonate ( $\text{TiO}(\text{C}_5\text{H}_7\text{O}_2)_2$ ). The relative concentration of the metal acetylacetonate in the aqueous suspension preferably ranges from about 5 to 40 weight percent of the aqueous suspension. The wetting agent may be any  
15 relatively low foaming surfactant, including anionic, nonionic or cationic compositions, although nonionic is preferred. The wetting agent is typically added at about 0.24% by weight, but can range from about 0.01% to 1% or more. The aqueous medium is preferably distilled or deionized water. Aqueous  
20 suspensions for pyrolytic deposition of metal-containing films are described in U.S. Patent No. 4,719,127 particularly at column 2, line 16, to column 4, line 48, which is hereby incorporated herein by reference.

For both the CVD and the spray pyrolysis methods,  
25 the temperature of the substrate 22 during formation of the PASC coating 24 thereon must be within the range which will cause the metal containing precursor to decompose and form a coating having PASC activity (e.g. crystalline phase for metal oxide PASC coatings). As may be appreciated, the lower limit  
30 of this temperature range is largely affected by the decomposition temperature of the selected metal-containing precursor. For the above listed titanium-containing

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precursors, the minimum temperature of substrate 22 which will provide sufficient decomposition of the precursor is within the temperature range of about 400°C (752°F), about 500°C (932°F). The upper limit of this temperature range may be  
5 affected by the substrate being coated. For example where the substrate 22 is a glass float ribbon and the PASC coating 24 is applied to the float ribbon during manufacture of the float ribbon, the float glass may reach temperatures in excess of 1000°C (1832°F). The float glass ribbon is usually attenuated  
10 or sized (e.g. stretched or compressed) at temperature above 800°C (1472°F). If the PASC coating 24 is applied while the float glass before or during attenuation, the PASC coating 24 may crack or crinkle as the float ribbon is stretched or compressed respectively. Therefore, in the practice of the  
15 invention it is preferred to apply the PASC coating when the float ribbon is dimensionally stable e.g. below about 800°C (1472°F) for soda lime silica glass, and the float ribbon is at a temperature to decompose the metal-containing precursor e.g. above about 400°C (752°F).

20 Forming PASC coating 24 by CVD or spray pyrolysis methods is particularly well suited for practice during the manufacture of the glass float ribbon. In general, a glass float ribbon is manufactured by melting glass batch materials in a furnace and delivering the refined molten glass onto a  
25 bath of molten tin. The molten glass on the bath is pulled across the tin bath as a continuous glass ribbon while it is sized and controllably cooled to form a dimensionally stable glass float ribbon. The float ribbon is removed from the tin bath and moved by conveying rolls through alehr to anneal the  
30 float ribbon. The annealed float ribbon is then moved through cutting stations on conveyor rolls where the ribbon is cut into glass sheets of desired length and width. U.S. Patent

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Nos. 4,466,562 and 4,671,155 hereby incorporated by reference provide a discussion of the float glass process.

Temperatures of the float ribbon on the tin bath generally range from about 1093.3°C (2000°F) at the delivery  
5 end of the bath to about 538°C (1000°F) at the exit end of the bath. The temperature of the float ribbon between the tin bath and the annealing lehr is generally in the range of about 480°C (896°F) to about 580°C (1076°F); the temperatures of the float ribbon in the annealing lehr generally range from about  
10 204°C (400°F) to about 557°C (1035°F) peak.

U.S. Patent Nos. 4,853,257; 4,971,843; 5,536,718; 5,464,657; and 5,599,387 hereby incorporated by reference describe CVD coating apparatus and methods that may be used in the practice of the invention to coat the float ribbon during  
15 manufacture thereof. Because the CVD method can coat a moving float ribbon yet withstand the harsh environments associated with manufacturing the float ribbon, the CVD method is well suited to provide the PASC coating 24 on the float ribbon. The CVD coating apparatus may be employed at several points in  
20 the float ribbon manufacturing process. For example, CVD coating apparatus may be employed as the float ribbon travels through the tin bath after it exits the tin bath, before it enters the annealing lehr, as it travels through the annealing lehr, or after it exits the annealing lehr.

As may be appreciated by those skilled in the art, concentration of the metal-containing precursor in the carrier gas, the rate of flow of the carrier gas, the speed of the float ribbon (the "line speed"), the surface area of the CVD coating apparatus relative to the surface area of the float  
25 ribbon, the surface areas and rate of flow of exhausted carrier gas through exhaust vents of the CVD coating apparatus more particularly, the ratio of exhaust rate through the  
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exhaust vents versus the carrier gas input rate through the CVD coating unit, known as the "exhaust matching ratio" and the temperature of the float ribbon are among the parameters which will affect the final thickness and morphology of the PASC coating 24 formed on float ribbon by the CVD process.

U.S. Patent Nos. 4,719,126; 4,719,127; 4,111,150; and 3,660,061 hereby incorporated by reference describe spray pyrolysis apparatus and methods that may be used with the float ribbon manufacturing process. While the spray pyrolysis method like the CVD method is well suited for coating a moving float glass ribbon, the spray pyrolysis has more complex equipment than the CVD equipment and is usually employed between the exit end of the tin bath and the entrance end of the annealing Lehr.

As can be appreciated by those skilled in the art, the constituents and concentration of the pyrolytically sprayed aqueous suspension, the line speed of the float ribbon, the number of pyrolytic spray guns, the spray pressure or volume, the spray pattern, and the temperature of the float ribbon at the time of deposition are among the parameters which will affect the final thickness and morphology of the PASC coating 24 formed on the float ribbon by spray pyrolysis.

As is known by those skilled in the art, the surface of the glass float ribbon on the molten tin (commonly referred to as the "tin side") has diffused tin in the surface which provides the tin side with a pattern of tin absorption that is different from the opposing surface not in contact with the molten tin (commonly referred to as "the air side"). This characteristic is discussed in Chemical Characteristics of Float Glass Surfaces, Seiger, J., JOURNAL OF NON-CRYSTALLINE SOLIDS, Vol. 19, pp. 213-220 (1975); Penetration of Tin in The Bottom Surface of Float Glass: A Synthesis, Columbin L. et



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al., JOURNAL OF NON-CRYSTALLINE SOLIDS, Vol. 38 & 39, pp. 551-556 (1980); and Tin Oxidation State, Depth Profiles of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  and Oxygen Diffusivity in Float Glass by Mössbauer Spectroscopy, Williams, K. F. E. et al., JOURNAL OF NON-CRYSTALLINE SOLIDS, Vol. 211, pp. 164-172 (1997), which disclosures are hereby incorporated by reference. As may be appreciated by those skilled in the art, the PASC coating 24 may be formed on the air side of the float ribbon while it is supported on the tin bath (by the CVD method); on the air side of the float ribbon after it leaves the tin bath by either the CVD or spray pyrolysis methods and on the tin side of the float ribbon after it exits the tin bath by the CVD method. When the PASC coating 24 is formed on the tin side of float ribbon, it is expected that the tin and/or tin oxide present in glass surface will function as an SIDB layer 26 for the PASC coating 24 disposed thereon.

U.S. Patent Nos. 4,379,040; 4,861,669; 4,900,633; 4,920,006; 4,938,857; 5,328,768; and 5,492,750 hereby incorporated by reference describe MSVD apparatus and methods to sputter coat metal oxide films on a substrate, including a glass substrate. The MSVD process is not generally compatible with providing a PASC coating over a glass float ribbon during its manufacture because, among other things, the MSVD process requires negative pressure during the sputtering operation which is difficult to form over a continuous moving float ribbon. However, the MSVD method is acceptable to deposit the PASC coating 24 on substrate 22 e.g., a glass sheet. As can be appreciated by those skilled in the art, the substrate 22 may be heated to temperatures in the range of about 400°C (752°F) to about 500°C (932°F) so that the MSVD sputtered coating on the substrate crystallizes during deposition process thereby eliminating a subsequent heating operation.

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Heating the substrate during sputtering is not a preferred method because the additional heating operation during sputtering may decrease throughput. Alternatively the sputter coating may be crystallized within the MSVD coating apparatus directly and without post heat treatment by using a high energy plasma, but again because of its tendency to reduce throughput through an MSVD coater, this is not a preferred method.

The preferred method to provide a PASC coating using the MSVD method is to sputter a coating on the substrate, remove the coated substrate from the MSVD coater and thereafter heat treat the coated substrate to crystallize the sputter coating into the PASC coating 24. For example, but not limiting to the invention, with the MSVD method, a target of titanium metal sputtered in an argon/oxygen atmosphere having about 5-50%, preferably about 20% oxygen, at a pressure of about 5-10 millitorr to sputter deposit a titanium dioxide coating of desired thickness on the substrate 22. The coating as deposited is not crystallized. The coated substrate is removed from the coater and heated to a temperature in the range of about 400°C (752°F) to about 600°C (1112°F) for a time period sufficient to promote formation of the PASC crystalline form of titanium dioxide to render PASC activity. Generally at least an hour at temperature in the range of about 400°C (752°F) to about 600°C (1112°F) is preferred. Where the substrate 22 is a glass sheet cut from a glass float ribbon, the PASC coating 24 may be sputter deposited on the air side and/or the tin side.

The substrate 22 having the PASC coating 24 deposited by the CVD, spray pyrolysis or MSVD methods may be subsequently subjected to one or more post-PASC coating annealing operations to increase the self-cleaning activity of

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the PASC coating 24. It is believed that such post-PASC coating annealing may increase self-cleaning activity of the PASC coating 24 by promoting formation of the desired PASC crystalline phase. As may be appreciated, the time and temperatures of the anneal may be affected by several factors, including the makeup of substrate 22, the makeup of PASC coating 24, the thickness of the PASC coating 24, and whether the PASC coating 24 is directly on the substrate 22 or is one layer of a multilayer stack on substrate 22. It has been determined that where the substrate 22 is a piece of float glass and the PASC coating is a 400Å or 625Å thick anatase titanium dioxide formed by the spray pyrolysis method, that annealing the coating at 500°C (932°F) for up to 13 minutes increased PASC activity.

As discussed above, whether the PASC coating is provided by the CVD process, the spray pyrolysis process or the MSVD process, where the substrate 22 includes sodium ions that can migrate from substrate 22 into the PASC coating deposited on substrate 22, the sodium ions may inhibit or destroy the photocatalytic activity of the PASC coating by forming inactive compounds while consuming titanium e.g. by forming sodium titanates or by causing recombination of photoexcited charges.

It has been found that the PASC coating may be formed over a sodium ion containing substrate 22 without loss of photocatalytic activity by: 1) providing for a limited partial sodium ion poisoning of a portion of the PASC coating; and/or 2) providing an SiDB layer 26. Each method is discussed in detail below.

It has been found that when the thickness of the PASC coating exceeds a minimum threshold value, the PASC activity is not destroyed by sodium ion migration even though

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the PASC coating is deposited over the surface of a sodium-ion containing substrate while the substrate is at a temperature sufficient to cause migration of sodium ions from substrate into the PASC coating. While the mechanism for this result is not completely understood, it is believed that when the thickness of the PASC coating exceeds this minimum thickness, the sodium ions are able to migrate only through a fraction of the overall thickness of the PASC coating during the time period at which the temperature of substrate exceeds the temperature which permits sodium ion migration. Thereafter, when the temperature of substrate falls below that which causes sodium ion migration, the sodium ions migration stops or "freezes" in place, resulting in a thickness of the PASC coating opposite from the substrate surface free of sodium ion poisoning and able to maintain PASC activity. This minimum thickness of the PASC coating as may be appreciated by those skilled in the art varies with expected parameters such as, but not limited to, the time at which substrate is held above the temperature at which sodium ion migration occurs, the use to which the PASC article of manufacture is to be put and the degree of PASC activity desired or required. It has been found that for a CVD deposited titanium dioxide PASC coating over a piece of soda-lime-silica flat glass, the thickness of the PASC coating should be a minimum of about 250Å, preferably a minimum of about 400Å and more preferably a minimum of about 500Å to permit a sufficient portion of the PASC coating to remain free of sodium ion poisoning and retain its PASC activity.

Referring now to Fig. 2, in an alternative method of preventing sodium ion poisoning of the PASC coating, an SIDB layer 26 is provided between the PASC coating 24 and the substrate 22. The SIDB layer 26 may be the only layer between

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the PASC coating 24 and the substrate 22, or it may be one layer of a multilayer stack. Where a multilayer stack is employed, it is not required that the SIDB layer 26 be in contact with the substrate 22, provided the SIDB layer 26 is positioned between the PASC coating 24 and the substrate 22 to prevent sodium ion migration from the substrate 22 to the PASC coating 24.

The SIDB layer 26 may be formed of amorphous or crystalline metal oxides including but not limited to cobalt oxides, chromium oxides and iron oxides, tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, and mixtures thereof. Mixtures include but are not limited to magnesium/aluminum oxides and zinc/tin oxides. As can be appreciated by those skilled in the art, the metal oxide may include oxides, super-oxides or sub-oxides of the metal. While the thickness of the SIDB layer necessary to prevent sodium ion poisoning of the PASC coating varies with several factors including the time period at which a substrate will be maintained at temperatures above which sodium ion migration occurs, the rate of sodium ion migration from the substrate, the rate of sodium ion migration through the SIDB layer, the thickness of the PASC coating and the degree of photocatalytic activity required for a given application, typically for most applications, the SIDB layer thickness should be in the range of at least about 100Å, preferably at least about 250Å and more preferably at least about 500Å thick to prevent sodium ion poisoning of the PASC coating layer. The SIDB layer may be deposited over substrate 22 by CVD, spray pyrolysis, or MSVD methods. Where the spray pyrolysis or CVD methods are employed, the substrate 22 is preferably maintained at a temperature of at least about 400°C (752°F) to ensure

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decomposition of the metal-containing precursor to form the SIDB layer. The SIDB layer may be formed by other methods, including the sol-gel method, which sol-gel method as noted above is not compatible with the manufacture of a glass float ribbon.

A tin oxide SIDB layer may be deposited on substrate by spray pyrolysis by forming an aqueous suspension of dibutyltin difluoride ( $(C_4H_9)_2SnF_2$ ) and water and applying the aqueous suspension to the substrate via spray pyrolysis. In general, the aqueous suspension typically contains between 100 to 400 grams of dibutyltin difluoride per liter of water. Wetting agents may be used as suspension enhancers. During the preparation of the aqueous suspension, the dibutyltin difluoride particles may be milled to an average particle size of 1 to 10 microns. The aqueous suspension is preferably vigorously agitated to provide a uniform distribution of particles in suspension. The aqueous suspension is delivered by spray pyrolysis to the surface of a substrate which is at a temperature of at least about 400°C (752°F), preferably about 500°C to 700°C (932°F to 1292°F) whereupon the aqueous suspension pyrolyzes to form a tin oxide SIDB layer. As may be appreciated, the thickness of SIDB layer formed by this process may be controlled by, among other parameters, the coating line speed, the dibutyltin difluoride concentration in the aqueous suspension and the rate of spraying.

Alternatively the tin oxide SIDB layer may be formed by the CVD method on the substrate from a metal-containing precursor such as a monobutyltin trichloride vapor (hereinafter "MBTTCL") in an air carrier gas mixed with water vapor. The MBTTCL vapor may be present in a concentration of at least about 0.5% in the air carrier gas applied over substrate while the substrate is at a temperature sufficient to cause the

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deposition of a tin containing layer e.g. at least about 400°C (952°F), preferably about 500°C to 800°C (932°F to 1472°F) to form the tin oxide SIDB layer. As may be appreciated the thickness of the SIDB layer formed by this process may be controlled by, among other parameters, the coating line speed, the concentration of MBTTCL vapor in the air carrier gas and the rate of carrier gas flow.

An SIDB layer formed by the MSVD process is described in U.S. Patent Application Serial No. 08/597,543 filed February 1, 1996, entitled "Alkali Metal Diffusion Barrier Layer", hereby incorporated by reference, which discloses the formation of alkali metal diffusion barriers. The barrier layer disclosed therein is generally effective at thicknesses of about 20 to about 180Å, with effectiveness increasing as the density of the barrier increases.

The PASC coatings of the present invention are usually photocatalytically activated to self-cleaning upon exposure to radiation in the ultraviolet range e.g. 300-400 nanometers (hereinafter "nm") of the electromagnetic spectrum. Sources of ultraviolet radiation include natural sources e.g. solar radiation and artificial sources such as a black light or an ultraviolet light source such as the UVA-340 light source. When using artificial ultraviolet light sources under testing conditions where it is desired to determine how the PASC coating will react the natural ultraviolet radiation, as may be appreciated, the UVA-340 light source has a photon energy distribution which more closely matches that of sunlight than does the photon energy distribution of a black light source, allowing the UVA-340 light source to be used to more closely approximate how the PASC coating performs when exposed to sunlight.

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The ultraviolet radiation intensity is calibrated to an intensity of at least about 20 watts per square meter (hereinafter "W/m<sup>2</sup>") at the coated surface of the coating being tested. The intensity may be calibrated, for example, with an ultraviolet meter such as that sold under the trademark BLACK-RAY® by Ultraviolet Products, Inc., of San Gabriel, CA, under the model designation J-221. The light source is preferably positioned normal to the coating surface being tested.

The ultraviolet radiation source and the PASC coating may be positioned relative to each other such that the ultraviolet radiation passes first through the PASC coating then through the substrate (i.e. the front or "coating side"). Where the substrate passes ultraviolet radiation therethrough, the PASC coating and the ultraviolet radiation source may be positioned relative to each other such that the ultraviolet radiation passes first through the substrate and then through the PASC coating (i.e. the back or "substrate side"). In still another embodiment, one or more ultraviolet radiation source may be positioned on each side of the substrate having a PASC coating on one or both of the surfaces.

As may be appreciated, it is difficult to define with specificity a preferred ultraviolet radiation source or ultraviolet radiation intensity or ultraviolet radiation source/PASC coating/substrate relative positioning because many factors affect such considerations. These factors include, among others: the purpose for which the PASC coating is employed e.g. indoor or outdoor use; the selected ultraviolet radiation source e.g. natural or artificial; seasonal or geographic effects where the ultraviolet radiation source is natural; the desired or expected duration of ultraviolet radiation exposure; the incident angle of the ultraviolet radiation with the surface of the PASC coating;



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the rate of PASC activity expected or desired; the degree to which the ultraviolet radiation may be reflected or absorbed by the substrate and/or any other coatings or layers present over the substrate or over PASC coating; the contaminants sought to be removed; the thickness of the PASC coating; the composition of the PASC coating; the potential for sodium ion poisoning; and the presence or absence of an SIDB layer. However, it has been found that an ultraviolet radiation intensity within the range of about 5 to 100 W/m<sup>2</sup>, preferably at least about 20 W/m<sup>2</sup>, as measured at the surface of PASC coating from an ultraviolet radiation source positioned over the surface of the PASC coating will produce sufficient intensity to cause satisfactory PASC activity for many self-cleaning applications.

It is useful to be able to measure and compare the PASC effectiveness or activity of PASC coatings in order to evaluate the PASC activity of a PASC coating. A known, readily available organic contaminant may be applied over the PASC coating, and upon photocatalytically activating the PASC coating, the ability of the PASC coating to remove the organic contaminant may be observed and measured. Stearic acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COOH, is a model organic "contaminant" to test the PASC activity of PASC coatings, because stearic acid is a carboxylic acid with a long hydrocarbon chain and is therefore a good "model molecule" for those present in common contaminants such as household oils and dirt. The stearic acid may be applied over the PASC coating as a thin test film by any convenient technique including dipping, spraying, spin coating. Generally stearic acid test films ranging from about 100Å to about 200Å thick provide an adequate test film. The stearic acid may be applied as a stearic acid in methanol solution and a solution having a concentration of about 6 x

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$10^{-3}$  moles of stearic acid per liter of solution has been found to be satisfactory.

The PASC activity of PASC coatings may be estimated qualitatively by overcoating PASC coating with a stearic acid film (the film generally appears as a light brown coating when applied over the PASC coating) exposing the stearic acid film to ultraviolet radiation at a desired intensity for a desired interval, and examining the stearic acid film with the unaided eye for either the complete disappearance of the stearic acid test film or for a decrease in the darkness of the stearic acid film in comparison to a portion of the stearic acid film applied over the PASC coating but not exposed to ultraviolet radiation.

The PASC activity of PASC coatings may also be measured quantitatively by measuring the integrated intensity of the carbon-hydrogen (hereinafter "C-H") stretching vibrational absorption bands of the stearic acid present on the PASC coating. The integrated intensity is commensurate with the thickness of stearic acid film remaining on the surface of the PASC coating, and removal of the stearic acid film by photocatalytically-activated self-cleaning is expected to result in a drop in the C-H stretching vibrational band intensity. The C-H bonds present in the stearic acid absorb infrared radiation which unlike ultraviolet radiation, does not photocatalytically activate the PASC coating. This absorption generally occurs between 2800 and 3000  $\text{cm}^{-1}$  wave numbers, and may be measured with a Fourier Transform Infrared Spectrophotometer (hereinafter "FTIR Spectrophotometer"). The FTIR may be equipped with a detector such as a deuterated triglycine sulfate detector (hereinafter "DTGS detector") or a mercury-cadmium-telluride detector (hereinafter "MCT detector"). The MCT detector is preferred as it provides a

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much higher signal-to-noise ratio than the DTGS detector. This can be important where the substrate and/or other coatings in addition to the PASC coating to absorb the infrared radiation which is used by the spectrophotometer to  
5 generate the absorption spectrum. When the infrared radiation is absorbed by the substrate and/or other coatings, the intensity of the infrared radiation beam that passes through the stearic acid film, PASC coated, and substrate to the detector is significantly reduced. Combining this with the  
10 low concentration of stearic acid present on the surface of the PASC coating (which produces a very weak infrared radiation absorption feature) and the resultant infrared radiation signal is not particularly intense. Therefore, an instrument equipped with the MCT detector provides a spectrum  
15 in which the signal-to-noise ratio is about an order of magnitude higher than those equipped with DTGS detectors. When measuring the PASC activity of a stearic acid test film deposited over films and substrates through which the infrared radiation beam may pass, the infrared radiation beam may be  
20 directed through the films and substrate onto the detector positioned on the opposite side of the sample being tested. Where the films or substrates will not permit the passage of infrared radiation therethrough, the infrared radiation beam may be directed at an angle over the surface, passing through  
25 the stearic acid test film and reflecting off of the substrate as opposed to passing therethrough onto the detector. This latter method is known as reflection IR spectroscopy.

A PASC reaction rate may be determined for a PASC coating by measuring the rate at which the PASC coating reacts  
30 to remove the stearic acid film thereon when the PASC coating is exposed to actinic radiation. More particularly, the rate of decrease in the integrated intensity of the C-H stretching

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vibrational feature (directly proportional to surface coverage) with accumulated time of exposure to actinic (hereafter assumed to be ultraviolet) radiation provides the PASC reaction rate. For example, an initial PASC activity is measured with the FTIR spectrophotometer for a stearic acid test film present on a PASC coating. The PASC coating may or may not have been exposed to ultraviolet radiation for this initial PASC activity measurement. The stearic acid coated PASC coating is then exposed to ultraviolet radiation for a measured interval of time, at the end of which a second PASC activity measurement is made with the FTIR spectrophotometer. The integrated intensities of the C-H stretching vibrations in the second measurement is expected to be lower than in the first, due to the fact that a portion of the stearic acid test film was removed with the exposure to ultraviolet radiation. From these two measurements, a curve may be plotted of integrated intensity of C-H stretching vibrations versus time, the slope of which provides the PASC reaction rate. While two points will suffice to provide a curve, it is preferred that several measurements are taken during the course of a PASC activity measurement to provide a more accurate curve. While the duration of exposure to ultraviolet radiation between FTIR measurements may be kept constant or may be varied when accumulating more than two PASC activity measurements (as it is the cumulated time of exposure to ultraviolet radiation that is used to plot the curve), the intensity and orientation (coating side or substrate side) of the ultraviolet radiation should be kept constant for all PASC measurements taken when determining the PASC reaction rate.

The PASC reaction rate may be reported in the units of  $\text{cm}^{-1} \text{ min}^{-1}$ , where the higher the value indicates a greater PASC activity. There is no absolute rate which renders a PASC

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coating "acceptable" or "unacceptable" because whether the PASC coating has an acceptable level of PASC is largely determined for the purpose for which the PASC coated article is used and the performance standards selected in connection  
5 with that purpose. For most applications, a PASC activity of at least about  $2 \times 10^{-3}$ , more preferably at least about  $5 \times 10^{-3}$   $\text{cm}^{-1} \text{min}^{-1}$  is desired.

It is also useful to measure the thickness of the PASC coatings in order to meaningfully determine and compare  
10 the PASC activity of PASC coatings prepared in accordance with the present invention because PASC coating thickness may affect photocatalytic activity as demonstrated in the examples below. The thicknesses of the PASC coating 24 and/or SIDB layer 26, if present may be determined by either Variable  
15 Angle Spectroscopic Ellipsometry (hereinafter "VASE") or from profilometer measurements of a deletion edge in the measured film, or may be estimated from interference colors, as is known in the art.

The particle size of the PASC coating 24 and/or SIDB  
20 layer 26, if present may be calculated from X-ray Diffraction (hereinafter "XRD") data using the Scherrer relationship. This relationship is known in the art and a discussion of it may be found in Chapter 9 of X-RAY DIFFRACTION PROCEDURES FOR POLYCRYSTALLINE AND AMORPHOUS MATERIALS, Klug and Alexander,  
25 John Wiley & Sons, Inc. (1954).

The following examples of the present invention are presented for illustration and the invention is not limited thereto.

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EXAMPLE 1*2100Å Thick PASC Coating Formed By The CVD Process*

The PASC activity of a titanium dioxide PASC coating having a thickness of about 2100Å was investigated as follows.

5 A PASC coating was deposited using the CVD process on substrate 22 which was the air side of a piece of soda-lime-silica float glass sold under the trademark SOLEX® glass by PPG Industries, Inc., of Pittsburgh, Pennsylvania. With reference to Fig. 3, the piece of Solex® glass measured  
10 approximately 5.5 inches wide by 12 inches long by .016 inches thick (14 cm wide by 30.5 cm long by 0.4 cm thick) and was coated with a titanium dioxide PASC coating using a CVD coater 88 as shown in Fig. 3. The CVD coater 88 generally consists of three zones shown in Fig. 3 separated by vertical dashed  
15 lines 90 and 92. The three zones include a preheat zone 94, a coating zone 96 and an annealing zone 98. The piece of Solex® glass, designated hereinafter as substrate 22, was moved through the three zones on an endless conveyor 102 in the direction of arrow 104.

20 The substrate 22 was moved into the preheat zone 94 and was preheated to a temperature of about 649°C (about 1200°F) by a plurality of heaters 106 spaced above and below the conveyor 102. The substrate 22 was moved by the conveyor 102 into the CVD coating zone 96. As may be appreciated, the  
25 CVD coating zone 96 includes at least one coating unit 97. In order to deposit more than one coating in succession, coating zone 96 may include a plurality coating units 97. The coating unit 97 includes supporting sub-systems and controls such as a gas delivery sub-system, a liquid delivery sub-system,  
30 temperature controls, an exhaust sub-system and controls and a temperature and pressure monitoring sub-system, none of which is shown. The gas delivery sub-system controls the flow of

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carrier gas to the surface of the substrate 22. Nitrogen gas was used as a carrier gas. The inlet nitrogen stream was controlled to a temperature of 113°C (about 235°F) by heaters not shown. NH<sub>3</sub> was included in the carrier gas at 20% of the total flow rate. The exhaust flow rate was 125% match of the inlet flow rate. The metal-containing precursor used to deposit the titanium dioxide PASC coating on the substrate 22 was TTIP which was present at 0.4% by volume of total flow and was also supplied at a temperature of about 113°C (about 235°F). The total flow of N<sub>2</sub>, NH<sub>3</sub> and TTIP vapor through the CVD coater 88 was 75 standard liters per minute (slm). The line speed of the conveyor 102 was about 50 inches (127 cm) per minute, and the coating unit slot width was about 3/16 inch (0.48 cm). The substrate 22 was maintained at a temperature of about 554°C (1030°F) while under the coating unit 97, while a coating 24 was deposited on the substrate 22 to form coated sample 100. An approximately 2100Å thick (as measured by VASE) titanium dioxide PASC coating 24 was formed on coated sample 100.

The coated sample 100 was then advanced to the annealing zone 98 where it was annealed from an initial temperature of about 549°C (1020°F) to a final temperature of about 121°C (250°F) over a period of about 26 minutes.

The PASC coated sample 100 was subjected to XRD analysis. The particle size of the PASC coating 24 was determined to be about 309Å as calculated using the Scherrer relationship. The coated sample 100 showed strong peaks in the XRD pattern corresponding to anatase titanium dioxide.

The PASC coated sample 100 was then overcoated with a stearic acid test film to measure its photocatalytic activity. A stearic acid/methanol solution having a concentration of about  $6 \times 10^{-3}$  moles of stearic acid per liter

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of solution was applied by pipetting the stearic acid solution at a rate of about 2 ml/10 seconds over the center of the sample 100, while the coated sample 100 was spinning at a rate of about 1000 revolutions per minutes, whereupon the stearic acid flowed across the surface of the coated sample 100, by centrifugal force to provide a stearic acid film of generally uniform thickness on the surface of the coated sample 100, ranging from about 100 to 200Å in thickness. The term "generally" is used in the foregoing because the thickness of the stearic acid layer was not constant along the length of the coated sample 100, but was thickest at the ends of the coated sample 100 and thinnest at the center of the coated sample 100 due to the applied centrifugal force. As may be appreciated, the described stearic acid solution concentrations, spin rate, sample size and pipetting rate may be modified to obtain stearic acid coatings of desired thicknesses. Under the above-described parameters, the average thickness of the stearic acid test film was about 150Å, as determined by calibration of IR intensity with quartz crystal microbalance.

The stearic acid test film/titanium dioxide PASC coated sample 100 was exposed to ultraviolet radiation from a black light source normal to coating side of the coated sample 100, providing an intensity of about 20 W/m<sup>2</sup> at the surface of the PASC coating 24 for about a cumulated 30 minutes to induce photocatalytically-activated self-cleaning of the stearic acid test film. Periodic FTIR spectrophotometer measurements were made over the cumulated 30 minute ultraviolet light exposure period using an FTIR spectrophotometer equipped with an MCT detector to quantitatively measure photocatalytic activity. More particularly, the stearic acid test film/PASC coated sample 100 was exposed to ultraviolet radiation for a measured



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period of time, after which the coated sample 100 was placed in the FTIR spectrophotometer where the integrated area under the C-H absorption band of stearic acid was measured to determine PASC activity. The coated sample 100 was again  
5 exposed to ultraviolet radiation for an additional measured period of time to remove additional stearic acid, after which another FTIR measurement was made. This process was repeated, and a plot of the integrated IR absorption intensity of the C-H stretching vibrations versus cumulated time of exposure to  
10 ultraviolet light was obtained, the slope of which provided the PASC rate for the stearic acid test film/titanium dioxide PASC coated sample 100. As may be appreciated, all FTIR measurements were taken over about the same area of coated sample 100 in order to minimize the effect of variations in  
15 the thickness of the stearic acid test film as described above. The photocatalytic reaction rate was determined to be  $3.53 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  which is approaching the values for PASC coated substrates which contain little or no sodium ions (e.g. quartz glass substrates) indicating that the 2100Å thickness  
20 of the titanium dioxide PASC coating was sufficient to overcome sodium ion poisoning.

#### EXAMPLE 2

##### *700-800Å Thick PASC Coating Formed By The CVD Process*

25 A titanium dioxide PASC coating 24 having a thickness of about 700-800Å was deposited on a glass substrate via the CVD process in the same manner as in Example 1, with the following exceptions.

The glass composition used in Example 2 was 3 mm  
30 (.12 inch) thick clear (i.e. low iron soda lime silica) glass. The preheat temperature of Example 2 was 593°C (1100°F). The TTIP concentration in Example 2 was 0.1% with a total flow

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rate of 50 slm.  $\text{NH}_3$  was included in the carrier gas at 24% of the total flow rate. The line speed was 30 inches per minute (76.2 cm per minute). The slot width was 1/16 inch. The thickness of the titanium dioxide PASC coating 24 was

- 5 estimated from interference colors, a technique known in the art of thin film thickness measurement, and determined to be within the range of about 700 to 800 Angstroms.

A stearic acid test film was applied over the titanium dioxide PASC coating in the same manner as set forth  
10 in Example 1, and after exposure to UV light in the manner described in Example 1 with periodic FTIR spectrophotometer measurements of PASC activity over a 33-hour cumulative period. The photocatalytic reaction rate was determined to be about  $0.17 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

- 15 The decreased PASC activity of Example 2 is believed to arise from the difference in titanium dioxide coating thickness between Examples 1 and 2, (about 2100Å versus about 700-800Å, respectively). More particularly, it is believed that the PASC reaction rate of Example 2 was lower than that  
20 of Example 1 due to the increased depth of sodium ion diffusion into the titanium dioxide coating of Example 2 as a larger percentage of the total thickness of the titanium dioxide PASC coating for the titanium dioxide PASC coating of Example 2 than that of Example 1. It is believed that sodium  
25 ions migrated from the glass sample into the PASC coating of Example 2 in annealing Lehr 44. One conclusion that may be drawn from a comparison of Examples 1 and 2 is that in the absence of an SIBD layer, thicker PASC coatings are less susceptible to sodium ion poisoning, thus maintaining higher  
30 PASC activity.

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EXAMPLE 3*PASC Coating Over An SIDB Layer Formed By The CVD Process*

In this example the affect of the presence of a tin dioxide SIDB layer on PASC activity was investigated. More particularly a tin dioxide SIDB layer was formed over the air side of four pieces of float glass and certain physical characteristics of the SIDB layer were investigated. Thereafter, sixteen additional pieces of float glass were provided with a tin dioxide SIDB layer by the CVD process, each of which tin dioxide SIDB layer was in turn overcoated with a titanium dioxide PASC coating by the CVD process. One sample was cut from each of the sixteen PASC coated/SIDB layer coated/float glass pieces, and these sixteen samples were overcoated with a stearic acid test film. The sixteen stearic acid test film coated/titanium dioxide PASC coated/tin dioxide SIDB layer coated/samples were exposed to ultraviolet radiation and the PASC reaction rates for the samples were determined.

20 3A. INVESTIGATION OF SIDB LAYER

An SIDB layer was deposited via the CVD process using the CVD apparatus described in Example 1 on the air side of four pieces of glass cut from a soda-lime-silica float glass ribbon which measured about 5 inches by 12 inches by 0.16 inch thick (12.7 cm by 30.48 cm by 0.4 cm). More particularly, the SIDB layer was a tin dioxide SIDB layer and the affect of the metal-containing precursor concentration, water vapor concentration, CVD line speed, preheat temperatures and SIDB layer thickness on the tin dioxide SIDB layer were investigated. The metal-containing precursor used to form the tin oxide SIDB layer by the CVD process on all

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four glass pieces was a MBTTCL vapor, which was mixed with water vapor in an air carrier gas.

A first of the four glass pieces was coated by the CVD process and apparatus of Example 1 with a tin oxide SIDB layer by directing an MBTTCL vapor at about a 1.5% concentration and a water vapor concentration of about 1.5% in an air carrier gas toward the air side of the glass piece. The preheat temperature was about 648°C (1200°F) and the line speed was about 50 inches (127 cm) per minute for this glass piece. The tin oxide SIDB layer formed thereby was about 3500Å thick as determined by VASE. The resistivity and particle size of the SIDB layer were measured and found to be about  $4.6 \times 10^{-3}$  ohm-cm and 198Å respectively.

A second glass piece was similarly coated with a tin oxide SIDB layer, however the line speed was decreased to about 20 inches (50.8 cm) per minute and the MBTTCL vapor concentration was decreased to about 0.5% and the water vapor concentration was decreased to about 0.5% in the air carrier gas. The preheat temperature was maintained at about 648°C (1200°F). The tin oxide SIDB layer formed thereby was about 4340Å thick as determined by VASE. The resistivity was found to be about  $3.9 \times 10^{-3}$  ohm-cm and particle size was about 185Å.

A third of the glass pieces was similarly coated with a tin oxide SIDB layer, however, preheat temperature was decreased to about 480°C (900°F), while the line speed was increased to about 50 inches (127 cm) per minute. The MBTTCL concentration was about 1.5%, water vapor concentration about 1.5% in an air carrier gas. The resulting tin oxide SIDB layer had a coating thickness of about 1000Å as determined by VASE and had a resistivity of about  $3.8 \times 10^{-2}$  ohm-cm and a particle size of about 59Å.

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A fourth glass piece was similarly coated with a tin oxide SIDB layer, however while the preheat temperature was maintained at about 480°C (900°F), the line speed was decreased 20 inches (50.8 cm) per minute. MBTTCL concentration was about 0.5%, and water concentration was about 0.5% in an air carrier gas. The tin oxide SIDB layer was about 1010Å thick as determined by VASE, and had a resistivity of about  $2 \times 10^{-2}$  ohm-cm and a particle size of about 78Å.

From the foregoing it was concluded that within the temperature ranges, concentrations, line speeds and SIDB layer thicknesses set forth, while resistivity or particle size may vary, all four glass pieces were found to have had a cassiterite structure.

**3B. FORMATION OF TITANIUM DIOXIDE PASC COATING FORMED OVER TIN OXIDE SIDB LAYER BY THE CVD PROCESS**

Sixteen additional float glass pieces measuring 5 inches by 12 inches by 0.16 inch thick (12.7 cm by 30.48 cm by 0.4 cm) were each coated with the CVD coater and process as generally described in Example 3A with a tin oxide SIDB layer and were then further coated with a titanium dioxide PASC coating using the CVD coating apparatus and process as generally described in Example 1. For this coating operation, the on-line CVD process used a pair of consecutive coating units (one for the SIDB layer and one for the PASC coating). The PASC coating over the SIDB layer makes separate analysis of the SIDB layer difficult if not impossible, therefore, it was assumed that the PASC overcoated tin oxide layers had the same properties as the non overcoated tin oxide layers described in Section 3A above, although both the SIDB layers and the PASC coatings were applied to the sixteen glass pieces

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under a variety of specific coating parameters as described in detail below and as set forth in Table 1 below.

Generally, the sixteen tin oxide SIBD layers were deposited from a metal-containing precursor of a MBTTCL vapor in an air carrier gas mixed with water vapor, also carried in air. The MBTTCL vapor temperature was maintained at about 160°C (320°F). The total flow rate was 60 slm, and the exhaust matching ratio was 115%. The slot width was 0.16 cm (1/16 inch). The specific coating parameters which were varied for the SIBD layers formed in this example included preheat zone 94 temperature, line speed, MBTTCL concentration, water vapor concentration and SIBD layer thickness. Shown in Table 1 below are the tin dioxide SIBD layer coating parameters and expected SIBD layer thicknesses for each of the sixteen glass pieces. Actual thickness measurements were not taken; expected thicknesses are based on the results obtained in section 3A above. The sixteen pieces are separated in Table 1 into four groups of four substrates each, based upon preheat temperature and line speed.

TABLE 1						
<u>SnO<sub>2</sub> SODIUM ION DIFFUSION BARRIER LAYER CVD COATING PARAMETERS</u>						
Group No.	Sample No.	Preheat Temp. °F	Line Speed in/min	H <sub>2</sub> O Conc Vol. %	MBTTCL Conc %	Expected SIBD Layer Thickness Å
I	1	900	20	0.5	0.5	1010
	2	900	20	0.5	0.5	1010
	3	900	20	0.5	0.5	1010
	4	900	20	0.5	0.5	1010
II	5	900	50	1.5	1.5	1000
	6	900	50	1.5	1.5	1000
	7	900	50	1.5	1.5	1000
	8	900	50	1.5	1.5	1000
III	9	1200	20	0.5	0.5	4340
	10	1200	20	0.5	0.5	4340
	11	1200	20	0.5	0.5	4340
	12	1200	20	0.5	0.5	4340
IV	13	1200	50	1.5	1.5	3500
	14	1200	50	1.5	1.5	3500
	15	1200	50	1.5	1.5	3500
	16	1200	50	1.5	1.5	3500

Each of the SIBD coated sixteen glass pieces was in turn overcoated with a titanium dioxide PASC coating deposited from the second CVD coating unit located downstream of the first SIBD coating unit through which a metal-containing precursor of TTIP vapor carrier in a nitrogen (N<sub>2</sub>) carrier gas was directed over the SIBD layer coated surface of the glass pieces. Ammonia (NH<sub>3</sub>) was added to the TTIP/carrier gas mixture of eight of the sixteen glass pieces. The carrier gas for all sixteen pieces was maintained at a temperature of about 113°C (235°F). The sixteen pieces were annealed as in

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Example 1. The TTIP vaporizer temperature was maintained at about 104.4°C (220°F). Shown in Table 2 below are the titanium dioxide PASC coating parameters for the sixteen glass pieces. The sixteen glass pieces are separated in Table 2 into four  
5 groups of four pieces each based upon preheat temperature and line speed.



TABLE 2  
 TiO<sub>2</sub> PHOTOCATALYTICALLY-ACTIVATED SELF-CLEANING COATING PARAMETERS

Group No.	Sample No.	Preheat Temp. °F*	Line Speed in/min	Total Flow Rate L/min	Exhaust Matching %	TTIP Conc. %	NH <sub>3</sub> Conc. %	Slot Width Inches
I	1	900	20	35	105	0.1	0	1/16
	2	900	20	75	105	0.4	0	3/16
	3	900	20	35	125	0.4	20	1/16
	4	900	20	75	125	0.1	20	3/16
II	5	900	50	75	125	0.4	0	1/16
	6	900	50	35	125	0.1	0	3/16
	7	900	50	75	105	0.1	20	1/16
	8	900	50	35	105	0.4	20	3/16
III	9	1200	20	75	125	0.1	0	1/16
	10	1200	20	35	125	0.4	0	3/16
	11	1200	20	75	105	0.4	20	1/16
	12	1200	20	35	105	0.1	20	3/16
IV	13	1200	50	35	105	0.4	0	1/16
	14	1200	50	75	105	0.1	0	3/16
	15	1200	50	35	125	0.1	20	1/16
	16	1200	50	75	125	0.4	20	3/16

\*Preheat temperature here refers to the temperature of preheat zone 94. There was only one preheat operation, and the preheat temperatures listed here are the same preheat temperatures to which the 5 glass pieces were raised in the preheat zone as they moved through CVD coater 88 and first received the SiDB layer followed by the PASC coating, before entering the annealing zone 98.

Shown in Table 3 below are selected properties of each of the sixteen glass pieces after the PASC coating as described in Table 2 was applied. PASC coating thicknesses were not measured, but is expected to vary within each group due to variations in other deposition parameters such as line speed and precursor concentration. However, surface roughness and particle size of the PASC coating were determined in order to relate PASC activity to roughness and particle size. Surface roughness measurements were estimated based upon Atomic Force Microscope (hereinafter "AFM") measurements made of the PASC coating. It was found that there was a large variation in surface roughness and particle size and crystalline phase as a function of preheat temperature.

TABLE 3  
TiO<sub>2</sub> PHOTOCATALYTICALLY-ACTIVATED SELF-CLEANING COATING PROPERTIES

Group No.	Sample No.	Surface Roughness Rms	Particle Size Å	Crystalline Phase
I	1	4.13	*	not detected
	2	5.18	*	not detected
	3	7.87	*	anatase/rutile
	4	7.84	*	anatase/rutile
II	5	6.39	*	not detected
	6	4.38	*	not detected
	7	5.99	*	anatase/rutile
	8	7.50	*	not detected
III	9	14.71	*	not detected
	10	15.58	277	anatase
	11	23.08	121	anatase
	12	16.93	166	anatase
IV	13	13.13	216	anatase
	14	15.72	*	not detected
	15	14.52	*	weak anatase
	16	15.93	154	anatase

\*Particle size could not be calculated because either no peaks were detected for the anatase phase in the X-ray diffraction pattern (Samples 1, 2, 5, 6, 8, 9 and 14) or the peaks were too broad and weak to measure (Samples 3, 4, 7 and 15).

3C. DESCRIPTION OF TESTING OF PASC ACTIVITY OF THE SIXTEEN SUBSTRATES

A 1 inch by 4 inch (2.54 cm x 10.16 cm) sample or test strip was cut out of the center of each of the sixteen PASC coated/SIDB coated glass pieces. Each of the sixteen test strips was overcoated by spin coating with a stearic acid test film as described in Example 1. The sixteen test strips were then subjected to ultraviolet radiation from a black light source at an intensity of 20 W/m<sup>2</sup> over a 7-hour cumulative time period to induce photocatalytically-activated self-cleaning of the stearic acid test film.

Because the thickness of the stearic acid test film was found to vary along the length of the 1 inch by 4 inch (2.54 cm x 10.16 cm) test strips (i.e. a thicker stearic acid test film at each end of the test strips with a thinner stearic acid test film toward the center of each test strip, due to the centrifugal force affecting the stearic acid as it was dropped onto the center of spinning test strips as described above and as observed visually by changes in interference colors along the length of the test strips), photocatalytic activity was measured at each end of each of the sixteen test strips using the FTIR Spectrophotometer equipped with the MCT detector. The PASC reaction rates obtained from FTIR spectroscopy tests for each pair of tests conducted on each of the sixteen test strips are shown in Table 4.

**TABLE 4**  
**PHOTOCATALYTICALLY-ACTIVATED SELF-CLEANING ACTIVITY**  
**OF SIXTEEN TEST STRIPS**

Group No.	Sample No.	PASC Activity Rate	PASC Activity
		Left Side of Test Strip $\times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$	Right Side of Test Strip $\times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$
I	1	0.39	0.45
	2	0.32	0.28
	3	0.26	0.31
	4	0.4	0.39
II	5	0.5	0.57
	6	0.23	0.14
	7	0.27	0.22
	8	0.014	0.019
III	9	0.23	0.048
	10	0.96	0.77
	11	0.4	0.31
	12	0.52	0.43
IV	13	1.18	0.94
	14	0.73	0.77
	15	0.42	0.41
	16	0.25	0.35

It is evident from Table 4 that for certain test strips there is a very significant difference in the activities between the two ends of the test strip. This difference is believed to be related to non-uniformity of the thickness of the stearic acid layer on the test strip.

Referring to Table 4, there appears to be a lack of correlation between deposition conditions and PASC activity of the PASC coating over the SIDA layer. The three most active test strips as shown on Table 4 are Samples 13, 10 and 14 based

on the activities of the left sides of the test strips. These strips 13, 10 and 14 correspond to the higher preheat temperature of 1200°F (648.8°C). If ranked by PASC activity, the remaining 13 test strips show a mix of preheat temperatures, as well as other coating parameters in the ranking indicating that the presence of a sodium ion diffusion barrier layer may operate to prevent sodium ion poisoning of the PASC coating layer, and may permit greater latitude in coating conditions and parameters while still obtaining photocatalytic activity.

#### EXAMPLE 4

##### *PASC Coating Formed By Spray Pyrolysis*

In this example, glass pieces were coated by spray pyrolysis with titanium dioxide PASC coatings of differing thickness to investigate the affect of PASC coating thickness on PASC activity.

Three float glass pieces each 4 inch x 4 inch x 0.16 inch thick (10.16 cm x 10.16 cm x 4 mm) had the air side coated by spray pyrolysis with a titanium dioxide PASC coating.

The basic components of the pyrolytic spray equipment used to apply the PASC coating over the glass pieces are shown in Fig. 4. The spray pyrolysis equipment included a preheat zone 120 and a pyrolytic spray zone 122. A glass piece 126 was conveyed on a conveyor not shown into the preheat zone 120 where it was heated by a plurality of electric heaters 130 to a temperature in the range of about 600° to 700°C (1112°F to 1292°F). The glass piece 126 was then conveyed past an oscillating spray nozzle 132, which was positioned about 10 inches (25.4 cm) above the air side of the glass piece 126. An aqueous suspension of organometallic coating reactants 134 was maintained in suspension by agitator 136 in mixing chamber 138. The aqueous suspension 134 was moved through tubing 140 to spray nozzle 132 where it was mixed with compressed air in any

convenient manner (from a compressed air source 142 which was moved to spray nozzle 132 by tubing 144). A spray pattern 146 was formed as the aqueous suspension 134/compressed air mixture was sprayed from nozzle 132 onto the surface of the glass piece 126 and was pyrolyzed to form PASC coating 24 on the glass piece 126. The PASC coated glass piece 126 was allowed to cool in air.

For this example, the organometallic coating reactant selected was titanyl acetylacetonate and the rate of aqueous suspension delivered to the surface of the three glass pieces 126 was controlled so as to provide a PASC coating thickness on each glass piece. The thicknesses were 400Å, 725Å and 1000Å. All other coating parameters were held constant to determine the effect of PASC coating thickness on photocatalytic activity for a titanium dioxide PASC coating deposited by spray pyrolysis on clear float glass without an SiDB barrier layer.

Table 5 sets forth the specific coating parameters for this example.

TABLE 5  
COATING PARAMETERS FOR SPRAY PYROLYSIS OF TITANIUM DIOXIDE PASC COATING

Sample No.	Line Speed in/min	Coating Reactant	Concentration of Organometallic gms/l or rate	Delivery Rate ml/min	Atomizing Air Pressure lbs/in <sup>2</sup>	Deposition Temp. °C	TiO <sub>2</sub> Thickness Å	PASC Activity $\times 10^{-4} \text{ cm}^{-1} \text{ min}^{-1}$
A	75	titanyl acetyl-acetate	20 gms/ml	40 ml/min	50	672	400	2
B	75	titanyl acetyl-acetate	20 gms/ml	55 ml/min	50	677	725	2
C	75	titanyl acetyl-acetate	27 gms/ml	67 ml/min	50	688	1000	3



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After deposition of the titanium dioxide PASC coating, each of the three glass pieces was cut into four 1 inch x 4 inch (2.54 cm x 10.16 cm) test strips providing a total of 12 test strips.

5 One test strip from each of the three original glass pieces respectively was subjected to x-ray diffraction analysis. From this analysis all of the three glass pieces in this example were found by x-ray diffraction analysis to have strong x-ray diffraction lines matching anatase titanium dioxide.

10 To evaluate photocatalytic activity for the three glass pieces, one test strip from each of the three glass pieces respectively was overcoated with a stearic acid test film by the process described in Example 1. The three test strips were then exposed to ultraviolet radiation from a black light source  
15 positioned normal to the coated side of each test strip at an intensity of 20 W/m<sup>2</sup> over a seven hour cumulative time period. The photocatalytic reaction rate of each of the three test strips was determined quantitatively by FTIR spectroscopy using an MCT detector, as described above. The photocatalytic  
20 reaction rate for the three glass pieces is shown in Table 5.

From the foregoing it may be concluded that low but acceptable photocatalytic reaction rates may be obtained with PASC coatings formed by the spray pyrolysis technique, without sodium ion poisoning of the PASC coating. It may also be  
25 concluded that thicker PASC coatings give rise to higher PASC activity, as demonstrated by Sample C in Table 5.

EXAMPLE 5

Comparison Of PASC Coatings Formed By Spray Pyrolysis With And Without SIDB Layer and Investigation of the Affect of Post-PASC Coating Annealing

5

In this experimental matrix eight glass pieces were provided with a PASC coating by the spray pyrolysis method to evaluate the effect of the presence and absence of an SIDB layer, the effect of PASC coating thickness and the effect of substrate temperature during deposition of the PASC coating on the PASC reaction rate of PASC coatings.

More particularly, the air side of four of the eight glass pieces of 4 mm Solex® float glass were each coated with a 500Å thick tin dioxide SIDB layer which had been deposited by spray pyrolysis from an aqueous suspension of dibutyltin difluoride,  $(C_4H_9)_2SnF_2$  and a wetting agent. The tin dioxide SIDB layer was applied with the spray pyrolysis equipment and procedure described in Example 4. After coating with the SIDB layer, the glass samples were cooled to room temperature, these four glass pieces and the remaining four glass pieces were each coated with a titanium dioxide PASC coating over the SIDB layer, and were cooled to room temperature. It should be noted that the four SIDB layer coated glass pieces which were cooled to room temperature between the application of the SIDB layer and the PASC coating and then reheated prior to the application of the PASC coating, were prepared in this fashion because the laboratory pyrolytic spray equipment used in the experiment had only one spray pyrolysis station, thereby requiring changeover from a dibutyltin difluoride suspension (to provide the SIDB layer) to a titanyl acetylacetonate suspension (to provide the PASC coating). Such an intermediate cooling step would be eliminated in a preferred coater, e.g. two spray pyrolysis stations would be provided to

sequentially coat an SIBD layer and a PASC coating to a moving substrate, such as a continuous float ribbon of glass, without any such intermediate cooling step.

After all eight PASC coated glass pieces were cooled  
5 to room temperature, the glass pieces were overcoated with a stearic acid film described in Example 1 and the films were then exposed to ultraviolet radiation with a UVA 340 light source placed normal to the coating side of the stearic acid test film/PASC coated glass pieces to provide 20 W/m<sup>2</sup> intensity at  
10 the PASC coating surface. The PASC reaction rate for the removal of the stearic acid test film was determined quantitatively using the process as described in Example 1. This PASC reaction rate is recorded in Table 6 below under the column headed 0.00 min. It is to be noted that the 0.00 minute  
15 parameter refers to the fact that the glass piece having the PASC coating thereon after it was allowed to cool to room temperature and was not annealed; it does not refer to the accumulated time period of ultraviolet exposure.

The affect of annealing time on stearic acid removal  
20 was examined as follows. The residual stearic acid test film was washed off of the PASC coating of each of the eight glass pieces by wiping the surfaces with a methanol soaked wiping cloth until no stearic acid film or haze was observed. Each of the eight glass pieces was then in turn respectively placed in a  
25 furnace maintained at about 500°C (932°F) for about 3 minutes to heat the respective glass piece. The furnace heat was turned off, the furnace door was opened, and the respective glass piece was allowed to cool in the furnace to about room temperature. The slow cooling rate within the furnace provided the anneal.  
30 Each respective glass piece was then overcoated with a new stearic acid test film, exposed to ultraviolet radiation and the PASC reaction rate was determined in the same fashion as the non-annealed PASC coating described immediately above in this

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example. The residual stearic acid test film was again washed off the surface of each respective glass piece as described above, and respective each glass piece was subjected to additional heating for a ten minute period and allowed to slowly  
5 cool in the furnace in the same fashion, resulting in a 13 minute accumulated heating time period, whereupon a stearic acid test film was reapplied as described and the PASC reaction rate was determined as set forth above. The process was repeated yet another time to obtain a 73 minute accumulated heating time  
10 period followed by slow cooling in the furnace to provide the anneal.

The SIDB layer and PASC coating properties and PASC reaction rates versus accumulative annealing time period for the eight glass pieces (D-K) are shown in the following Table 6.

**TABLE 6**  
**PHOTOCATALYTIC ACTIVITY REACTION RATES OF PASC COATINGS**  
**WITH AND WITHOUT SODIUM-ION DIFFUSION BARRIER LAYER**

Sample	Barrier Layer	TiO <sub>2</sub> Thickness	Glass Temp. During TiO <sub>2</sub> Coating	Photocatalytic Activity* After Annealing at 500°C for			
				0.00** min	3 min	13 min	73 min
D	None	400Å	1145°F	0.72	1.05	1.94	***
E	None	625Å	1145°F	0.69	1.05	1.67	2.97
F	500Å SnO <sub>2</sub>	400Å	1147°F	2.39	5.02	7.39	***
G	500Å SnO <sub>2</sub>	625Å	1152°F	2.23	5.35	8.74	5.13
H	None	400Å	1260°F	2.05	6.59	5.14	***
I	None	625Å	1260°F	4.71	7.99	9.95	5.39
J	500Å SnO <sub>2</sub>	400Å	1300°F	2.4	5.26	3.73	***
K	500Å SnO <sub>2</sub>	625Å	1280°F	4.64	12.29	5.57	4.4

\*PASC reaction rate for removal of stearic acid ( $\times 10^{-3} \text{ cm}^2 \text{ min}^{-1}$ )

5

The results of the photocatalytic analysis shown in Table 6 suggest that a titanium dioxide layer thickness of about 625Å with no barrier layer (Sample I) can approach the PASC activity of a thinner 400Å PASC coating over an SIDB layer (Sample K). It should be noted that for Samples K, the SIDB layer underwent an intermediate cooling and subsequent reheating operation described, which reheating operation may have reduced the SIDB layer effectiveness for Sample K, which might otherwise have had a higher PASC activity.

15 Sample K of Table 6 also shows the significant impact annealing time can have on PASC reaction rate. After 3 minutes

anneal time the PASC activity of Sample K rose from about 4.64 to about  $12.29 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  but subsequently dropped with additional annealing. It is believed that the anatase phase of the titanium dioxide PASC coating was forming during annealing when the 3 minute time period PASC activity was measured and was forming without appreciable sodium ion poisoning due to the presence of the tin oxide in the SIDB layer. While not wishing to be bound to this particular theory, it is believed that continuing to anneal for too long a cumulated time period may induce sodium ion poisoning, despite the presence of the SIDB layer which would account for the decline in PASC activity of Sample K.

The above examples are offered to illustrate the present invention and are not intended to limit the invention.

While the above described methods of providing a PASC coating have been described in connection with providing such coatings on a continuous moving substrate e.g. a continuous float ribbon of glass during manufacture of the substrate, it is to be understood that these methods could also be utilized downstream of the substrate manufacturing process. For example, the PASC coatings could be provided on substrates including but not limited to glass substrates, as part of the processes to bend and/or temper the substrate. For example, where a glass substrate is heated for subsequent bending and/or tempering, the PASC coating with or without a SIDB layer may be applied by the spray pyrolysis or CVD or MSVD techniques described above prior to bending/tempering. The CVD and spray pyrolysis methods may be used as the glass substrate is heated to bending/tempering temperatures. The PASC coating, with or without an SIDB layer may be applied to the glass substrate in a post bending/tempering reheating operation by any of the CVD, spray pyrolysis or MSVD methods.

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It is believed that there are differences in the PASC coatings prepared by the sol-gel process and those prepared by the above-described methods. For example, it is expected that the PASC coatings prepared by the sol-gel process may be more porous, less dense, generally thicker, generally less applicable for use in a transparency and may tend to contain more OH groups than those prepared by the CVD or spray pyrolysis processes. As noted above, excess OH groups are undesirable because they may inhibit proper crystalline formation in the PASC coating which may in turn reduce PASC activity. It is expected that PASC coatings prepared by the CVD or spray pyrolysis methods would have a finer grain structure than those prepared by the sol-gel process.

Advantages of the present invention over the sol-gel method of forming PASC coatings include an ability to form a thin dense PASC film on a substrate as opposed to the much thicker, porous coatings obtained with the sol-gel coating method. Because the PASC coatings of the present invention are thin, they are aesthetically acceptable for use as a transparent coating on glass substrates. Still another advantage is that the method of providing a PASC coating according to the present invention avoids the need to reheat the substrate after application of the coating or coating precursor as is required with the presently available sol-gel method. Not only does this render the present method less costly and more efficient e.g. but not limited to less equipment costs, less energy costs, less production time but also, the opportunity for sodium ion migration and in turn sodium ion poisoning of the PASC coating of the present invention is significantly reduced. Further still, the method of the present invention is easily adapted to the formation of PASC coatings on continuous moving substrates, such as a glass float ribbon, where as the presently available sol-gel methods are not so easily adaptable.

Various modifications are included within the scope of the invention, which is defined by the following claims.



We claim:

1. A photocatalytically-activated self-cleaning article of manufacture comprising:

a substrate having at least one surface; and

5 a photocatalytically-activated self-cleaning coating deposited over the surface of the substrate by a process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis.

10

2. The photocatalytically-activated self-cleaning article of claim 1 wherein the photocatalytically-activated self-cleaning coating comprises a metal oxide selected from the group consisting of titanium oxides, iron oxides, silver oxides,  
15 copper oxides, tungsten oxides, aluminum oxides, silicon oxides, zinc stannates, molybdenum oxides, zinc oxides, strontium titanate and mixtures thereof.

3. The photocatalytically-activated self-cleaning article of claim 2 wherein the photocatalytically-activated self-cleaning coating comprises titanium dioxide selected from the group consisting of anatase titanium dioxide, rutile titanium dioxide, brookite titanium dioxide and mixtures thereof.

25

4. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is at least 200 Angstroms thick.

30

5. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is at least about 400 Angstroms thick.

6. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is at least about 500 Angstroms thick.

5 7. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating has a photocatalytic reaction rate of at least  $2 \times 10^{-3} \text{ cm}^{-1}\text{min}^{-1}$ .

10 8. The photocatalytically-activated self-cleaning article of claim 7 wherein said photocatalytic reaction rate is determined as the rate of removal of a stearic acid test film in the range of 100 to 200 Angstrom thick deposited over said photocatalytically-activated self-cleaning coating wherein said  
15 photocatalytic reaction rate is quantitatively determined as the slope of a curve formed by a plotting of a plurality of Fourier Transform Infrared Spectrophotometer measurements of the integrated intensity of carbon-hydrogen stretching vibrational absorption bands of the stearic acid test film versus an  
20 accumulated time of exposure of said photocatalytically-activated self-cleaning coating to ultraviolet radiation of a frequency within the range of about 300 to 400 nanometers provided by an ultraviolet radiation source positioned over said photocatalytically-activated self-cleaning coating and having an  
25 intensity of about 20 watts per square meter as measured at the surface of the photocatalytically-activated self-cleaning coating.

9. The photocatalytically-activated self-cleaning  
30 article of claim 8 wherein said ultraviolet radiation source is selected from the group consisting of a black light source and a UVA-340 light source.

10. The photocatalytically-activated self-cleaning article of claim 1 wherein the photocatalytically-activated self-cleaning coating is deposited directly over the substrate.

5 11. The photocatalytically-activated self-cleaning article of claim 1 further comprising at least one layer interposed between said photocatalytically-activated self-cleaning coating and the substrate.

10 12. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating comprises one layer of a multilayer stack of coatings deposited over the substrate and wherein the photocatalytically-activated self-cleaning coating is the  
15 uppermost layer of said multilayer stack.

13. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating comprises one layer of a multilayer stack  
20 of coatings deposited over the substrate wherein said photocatalytically-activated self-cleaning coating is a layer other than the uppermost layer of said multilayer stack.

14. The photocatalytically-activated self-cleaning  
25 article of claim 1 further comprising a sodium ion diffusion barrier layer disposed between the substrate and the photocatalytically-activated self-cleaning coating to inhibit migration of sodium ions from said substrate to said photocatalytically-activated self-cleaning coating.

30 15. The photocatalytically-activated self-cleaning article of claim 14 wherein the sodium ion diffusion barrier layer is deposited over the substrate by a process selected from

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the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis.

16. The photocatalytically-activated self-cleaning  
5 article of claim 14 wherein the sodium ion diffusion barrier layer is selected from the group consisting a crystalline metal oxide, an amorphous metal oxide and mixtures thereof.

17. The photocatalytically-activated self-cleaning  
10 article of claim 16 wherein the sodium ion diffusion barrier layer is selected from the group consisting of tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, cobalt oxides, chromium oxides, magnesium oxides, iron  
15 oxides and mixtures thereof.

18. The photocatalytically-activated self-cleaning  
article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 250 Angstroms thick.  
20

19. The photocatalytically-activated self-cleaning  
article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 400 Angstroms thick.

20. The photocatalytically-activated self-cleaning  
25 article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 500 Angstroms thick.

21. The photocatalytically-activated self-cleaning  
30 article of claim 1 wherein the substrate is selected from the group consisting of glass, plastic, metal, enamel and mixtures thereof.

22. The photocatalytically-activated self-cleaning article of claim 1 wherein said substrate is a glass substrate having a first major surface and an opposite major surface defined as a second major surface, the first major surface  
5 having a thin layer of a tin oxide diffused therein characteristic of forming a glass ribbon over a molten tin bath, at least one of the major surfaces having said photocatalytically-activated self-cleaning metal oxide coating deposited thereon.

10

23. The photocatalytically-activated self-cleaning article of claim 22 wherein the photocatalytically-activated self-cleaning coating further comprises a metal oxide selected from the group consisting of titanium oxides, iron oxides,  
15 silver oxides, copper oxides, tungsten oxides, aluminum oxides, silicon oxides, zinc stannates, molybdenum oxides, zinc oxides, strontium titanate and mixtures thereof.

24. The photocatalytically-activated self-cleaning  
20 article of claim 23 further comprising a sodium ion diffusion barrier layer disposed between the substrate and the photocatalytically-activated self-cleaning coating.

25. The photocatalytically-activated self-cleaning  
25 article of claim 24 wherein the sodium ion diffusion barrier layer is selected from the group consisting of tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, cobalt oxides, chromium oxides, magnesium oxides, iron  
30 oxides and mixtures thereof.

26. The photocatalytically-activated self-cleaning article of claim 22 wherein the glass substrate is selected from

the group consisting of a glass sheet and a continuous float glass ribbon.

27. A method for providing a titanium dioxide  
5 photocatalytically-activated self-cleaning coating over a continuous glass float ribbon during the manufacture of the float ribbon comprising the steps of:

manufacturing a continuous glass float ribbon  
having a first major surface and an opposite major  
10 surface defined as a second major surface, the first major surface having a thin layer of a tin oxide diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

- 15 positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the float ribbon has a temperature of at least about 400°C (752°F);

- 20 directing a metal oxide precursor selected from the group consisting of titanium tetrachloride, titanium tetraisopropoxide and titanium tetraethoxide in a carrier gas stream through said chemical vapor deposition apparatus over the surface of the float ribbon and annealing the float ribbon to produce a  
25 titanium dioxide photocatalytically-activated self-cleaning coating over the glass float ribbon.

28. A method for providing a titanium dioxide  
photocatalytically-activated self-cleaning coating over a  
30 continuous glass float ribbon during the manufacture of the float ribbon comprising the steps of:

manufacturing a continuous glass float ribbon  
having a first major surface and an opposite major

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surface defined as a second major surface, the first major surface having a thin layer of metal selected from the group consisting of tin, tin oxides and mixtures thereof diffused therein characteristic of forming the glass float ribbon on a molten tin bath; depositing a photocatalytically-activated self-cleaning coating over at least one of the major surfaces by positioning a spray pyrolysis coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the float ribbon has a temperature of at least about 400°C (752°F), directing an aqueous suspension of titanyl acetylacetonate and wetting agent in an aqueous medium through said spray pyrolysis coating apparatus over the surface of the float ribbon and annealing the float ribbon in air to produce a titanium dioxide photocatalytically-activated self-cleaning coating over the glass float ribbon.

29. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a Lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising: depositing a photocatalytically-activated self-cleaning coating over a surface of said float ribbon as the float ribbon is formed.

30. The method of claim 29 wherein said photocatalytically-activated self-cleaning coating is deposited by a process selected from the group consisting of spray pyrolysis and chemical vapor deposition.

5

31. The method of claim 29, the improvement further comprising depositing a sodium ion diffusion barrier layer over a surface of said float ribbon and depositing said photocatalytically-activated self-cleaning coating over said sodium ion diffusion barrier layer.

10

32. A method for the manufacture of a photocatalytically-activated self-cleaning article of manufacture comprising the steps of:

15

providing an article of manufacture having at least one surface;

depositing a photocatalytically-activated self-cleaning coating over the surface of the article of manufacture by a process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis.

20

33. The method of claim 32 wherein the article of manufacture is a glass sheet and said depositing step is performed during a process of modifying said glass sheet selected from the group consisting of bending and tempering of said glass sheet.

25

34. The method of claim 32 further comprising the step of depositing a sodium ion diffusion barrier layer over said surface and depositing said photocatalytically-activated self-cleaning coating over said sodium ion diffusion barrier layer whereupon said sodium ion diffusion barrier layer inhibits

30



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migration of sodium ions from the surface of said article to said photocatalytically-activated self-cleaning coating.

35. The method of claim 34 wherein the sodium ion  
5 diffusion barrier layer is deposited by a process selected from the group consisting of chemical vapor deposition, spray pyrolysis and magnetron sputtered vapor deposition.

36. The method of claim 35 wherein said step of  
10 depositing the sodium ion diffusion barrier layer is performed during a process of modifying said glass sheet selected from the group consisting of bending and tempering of said glass sheet.

37. The method of claim 32 further comprising the  
15 step of annealing said photocatalytically-activated self-cleaning coating to increase a photocatalytic reaction rate of said photocatalytically-activated self-cleaning coating.

38. The method of claim 37 wherein said annealing  
20 step includes raising said photocatalytically-activated self-cleaning coating to a temperature of about 500°C for a time period of at least about 3 minutes and controllably cooling said photocatalytically-activated self-cleaning coating.

39. The method of claim 38 wherein said  
25 photocatalytically-activated self-cleaning coating has a photocatalytic reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

40. The method of claim 38 wherein said  
30 photocatalytic reaction rate is determined as the rate of removal of a stearic acid test film in the range of 100 to 200 Angstrom thick deposited over said photocatalytically-activated self-cleaning coating wherein said photocatalytic reaction rate

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is quantitatively determined as the slope of a curve formed by a plotting of a plurality of Fourier Transform Infrared Spectrophotometer measurements of the integrated intensity of carbon-hydrogen stretching vibrational absorption bands of the

5 stearic acid test film versus an accumulated time of exposure of said photocatalytically-activated self-cleaning coating to ultraviolet radiation of a frequency within the range of about 300 to 400 nanometers provided by an ultraviolet radiation source positioned over said photocatalytically-activated self-

10 cleaning coating and having an intensity of about 20 watts per square meter as measured at the surface of the photocatalytically-activated self-cleaning coating.

1/1

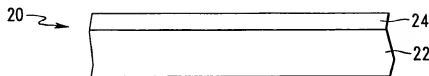


FIG. 1

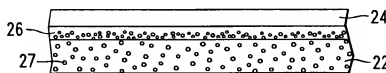


FIG. 2

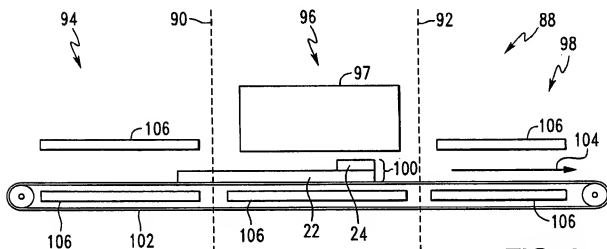


FIG. 3

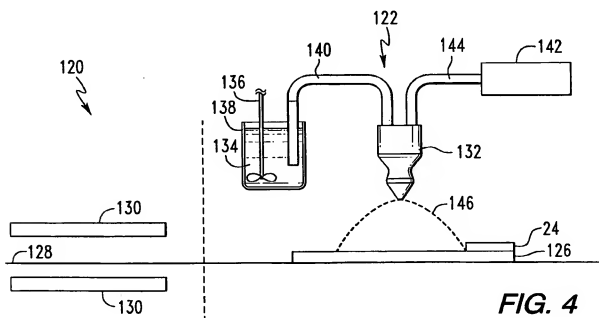


FIG. 4

# INTERNATIONAL SEARCH REPORT

national Application No

PCT/US 98/04785

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C03C17/245 C03C17/25 C03C17/34

According to International Patent Classification(IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category \* Citation of document, with indication, where appropriate, of the relevant passages

Relevant to claim No.

X	WO 97 07069 A (HARUVY YAIR :HELLER ADAM (US): PAZ YARON (US)) 27 February 1997 see page 2, line 20 - page 3, line 32 see page 7, line 20 - page 9, line 17 ---	1-40
X	MASANARI TAKAHASHI ET AL: "PT-TiO2 THIN FILMS ON GLASS SUBSTRATES AS EFFICIENT PHOTOCATALYSTS" JOURNAL OF MATERIALS SCIENCE, vol. 24, no. 1, January 1989, pages 243-246, XP000046035 see page 243 ---	1-10, 32, 39, 40

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

5 June 1998

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/04785

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WEINBERGER B R ET AL: "TITANIUM DIOXIDE PHOTOCATALYSTS PRODUCED BY REACTIVE MAGNETRON SPUTTERING" APPLIED PHYSICS LETTERS, vol. 66, no. 18, 1 May 1995, pages 2409-2411, XP000507607 see the whole document ---	1-10, 32, 39, 40
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 003, 31 March 1997 & JP 08 313705 A (SEIKO EPSON CORP), 29 November 1996, see abstract ---	1-10, 32, 39, 40
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 003, 31 March 1997 & JP 08 309202 A (BRIDGESTONE CORP), 26 November 1996, see abstract ---	1-10, 32, 39, 40
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 003, 31 March 1997 & JP 08 309204 A (BRIDGESTONE CORP), 26 November 1996, see abstract ---	1-10, 32, 39, 40
P, X	WO 97 10186 A (BOIRE PHILIPPE ; TALPAERT XAVIER (FR); SAINT GOBAIN VITRAGE (FR)) 20 March 1997 see page 2, paragraph 2 - page 3 see page 7, paragraph 3 - page 8, paragraph 2 see page 9, paragraph 2 - paragraph 4 see page 11, paragraph 5 - paragraph 6 ---	1-21, 32-40
P, A	EP 0 784 034 A (MATSUSHITA ELECTRIC WORKS LTD) 16 July 1997 see page 1, line 16 - page 3, line 25 -----	1-40

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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